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# Canadian Journal of Technology

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## A NEW METHOD FOR LIQUID FILM THICKNESS MEASUREMENT<sup>1</sup>

By A. M. PENNIE AND J. Y. BELANGER

### ABSTRACT

A new and simple method for liquid film measurement has been developed. The method is accurate and sensitive and employs a micrometer needle in conjunction with an electrical method for the detection of the point of contact.

### INTRODUCTION

During the study of evaporation in a falling film vacuum evaporator, it was found necessary to measure the thickness and velocity of the falling film. The evaporator was essentially a long vertical copper pipe 0.502 in. inside diameter, heated by a series of steam jackets spaced two inches apart. Feed of sodium carbonate was by spray onto the inner wall and the liquor descended filmwise, evaporating as it travelled down the wall. The controlled feed rate was measured by a calibrated rotameter and since the feed rate was known, a measure of the film thickness could then give the film velocity.

A search of the literature yielded no convenient or practical method for measuring film thickness so a method incorporating a micrometer screw gauge with electrical detection of the point of contact was employed.

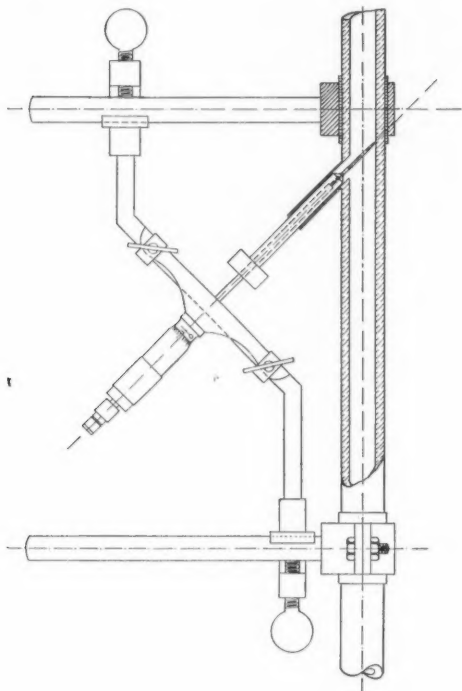
### APPARATUS

A micrometer depth gauge capable of reading to 1/10th of 1/1000 inch was modified by fitting a large sewing needle as an extension piece and insulating the rod by sleeving it with lucite. The needle was insulated, except for the point of contact, by dipping it in a thin solution of glyptal and acetone and then allowing it to dry.

An audio oscillator was connected in series with the micrometer via ear-phones. To check the accuracy and functioning of this measuring device a length of copper pipe of the same inside diameter was used to simulate the evaporator tube, and the apparatus was assembled as shown in Figs. 1 and 3. To ensure even film distribution over the entire pipe wall, an adjustable spray nozzle, as shown in Fig. 2, was employed. The space between the two faces can be adjusted so that, at all rates of feed, an even film is projected onto the tube-wall.

<sup>1</sup> Manuscript received September 20, 1951.

Contribution from Chemical Engineering Group of the Canadian Armament Research and Development Establishment, Valcartier, Que.



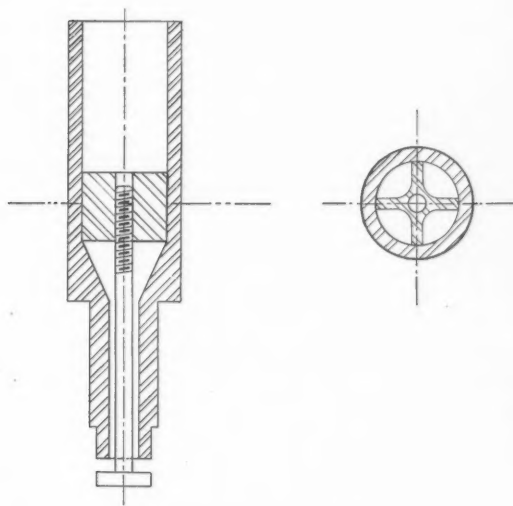
GENERAL VIEW OF THE APPARATUS SHOWING THE MEASURING DEVICE IN POSITION

FIG. 1

## EXPERIMENTAL

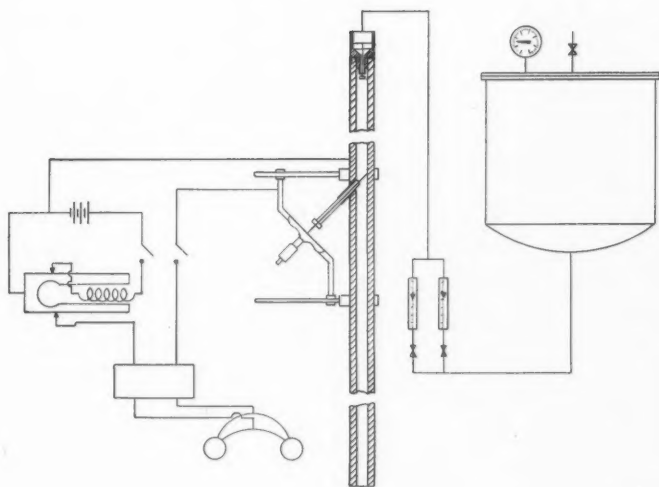
In all cases a clean filtered solution of 5% sodium carbonate in water was employed as the film medium. This was stored in a header tank and fed under pressure to the spray via the calibrated rotameters.

Before taking any measurements, the copper tube was cleaned twice with acetone, and a soft cotton cloth drawn through it to remove any dust or grease. The tube was rigidly fixed to a metal back plate and checked for verticality. The gauge was fixed in position by a set of suitable adjusting clamps and sealed from the side arm by means of a piece of close fitting rubber tubing. The needle bracket was insulated from the pipe by gaskets of sheet rubber. The micrometer was screwed carefully until it touched the wall and the sharp contact was heard. This reading was recorded as the zero, or wall reading. After withdrawing the needle to approximately the middle of the tube and adjusting the spray head, flow of sodium carbonate was started and controlled by means of a rotameter. Once steady flow had been achieved, the needle was carefully screwed forward until it made contact with the liquid film, and a



ADJUSTABLE SPRAY NOZZLE

FIG. 2



SCHEMATIC FLOW SHEET

FIG. 3

TABLE I  
FILM THICKNESS MEASUREMENTS AND CALCULATED DATA

Feed rate, lb. per min.	Film thickness measured at 45°, in.	Film thickness corrected value at 90°, in.	Area of flowing stream, ft. <sup>2</sup>	Velocity of film after one foot, ft. per sec.	Reynolds' Number
0.09	0.0070 0.0070 0.0070 0.0070	0.0050	0.000055	0.42	52
0.21	0.0127 0.0127 0.0127 0.0127	0.0090	0.000098	0.54	120
0.33	0.0170 0.0183 0.0183 0.0183	0.0130	0.000137	0.61	194
0.46	0.0198 0.0210 0.0210 0.0210	0.0150	0.000159	0.73	267
0.52	0.0240 0.0260 0.0240 0.0240	0.0170	0.000180	0.74	305
1.06	0.0280 0.0260 0.0260 0.0260	0.0184	0.000192	1.40	644
2.12	0.0300 0.0320 0.0310 0.0310	0.0220	0.000230	2.34	1235
2.65	0.0360 0.0370 0.0360 0.0350	0.0253	0.000264	2.54	1532
3.37	0.0400 0.0390 0.0410 0.0380	0.0283	0.000293	2.92	1955
4.40	0.0490 0.0470 0.0480 0.0490	0.0346	0.000349	3.18	2565
4.88	0.0500 0.0490 0.0470 0.0500	0.0353	0.000363	3.39	2800
5.60	0.0560 0.0580 0.0580 0.0590	0.0410	0.000412	3.46	3270

TABLE I. (Concl'd.)  
 FILM THICKNESS MEASUREMENTS AND CALCULATED DATA

Feed rate, lb. per min.	Film thickness measured at 45°, in.	Film thickness corrected value at 90°, in.	Area of flowing stream, ft. <sup>2</sup>	Velocity of film after one foot, ft. per sec.	Reynolds' Number
6.75	0.0600 0.0640 0.0640 0.0630	0.0452	0.000450	3.81	3930
8.96	0.0670 0.0700 0.0710 0.0700	0.0495	0.000489	4.65	5200
10.99	0.0780 0.0800 0.0770 0.0780	0.0552	0.000537	5.18	6390
13.15	0.0900 0.0890 0.0910 0.0900	0.0629	0.000603	5.50	7600
16.30	0.1080 0.1070 0.1080 0.1090	0.0764	0.000713	5.80	9440
19.00	0.1290 0.1300 0.1280 0.1290	0.0912	0.000817	5.89	11,050
22.50	0.1490 0.1490 0.1510 0.1490	0.1050	0.000910	6.27	13,000

steady note was heard on the earphones. Evidence of good even film was provided by the hollow cone of liquid emerging from the bottom of the tube. Several readings were taken at each feed rate and a series of values recorded for feed rates from 0.09 lb. per min. to 22.5 lb. per min. This range corresponds to film thicknesses of 0.005 in. to 0.105 in. Before each reading, the tube was cleaned with acetone and dried.

For low (2.5 lb. per min.) rates of feed it is satisfactory to insert the needle at right angles to the main flow, but as the rate increases above this value there is a tendency to flooding along the length of the needle, causing a short circuit. To obviate this, the needle was inserted at an angle of 45° to the flow and the necessary corrections made to all readings. A summary of the results is shown in Table I.

A series of readings was taken at 90° and 45° with the same rates of flow and the values are compared in Table II. Agreement can be observed in all cases.

TABLE II  
COMPARISON OF FILM THICKNESS MEASURED AT 45° AND 90°

Feed rate, lb. per min.	Film thickness measured at 45°, in.	Film thickness, corrected value at 90°, in.	Film thickness measured at 90°, in.
2.65	0.0360	0.0253	0.0260
	0.0370		0.0270
	0.0360		0.0260
	0.0350		0.0260
2.12	0.0300	0.0220	0.0230
	0.0320		0.0230
	0.0310		0.0240
	0.0310		0.0230
1.60	0.0280	0.0198	0.0200
	0.0270		0.0200
	0.0290		0.0200
	0.0280		0.0210
1.06	0.0280	0.0191	0.0190
	0.0280		0.0190
	0.0260		0.0190
	0.0260		0.0190

Further evidence of uniform film conditions prevailing during measuring was given by the observation that after reading the film thickness, the sound ceased when the needle was withdrawn. When the needle re-entered the film on the opposite side contact was again established. No sound was heard while the needle was passing through the air space in the center of the tube.

To obtain the wide variety of feed rates necessary, two rotameters were operated in parallel. A limiting value for accurate and consistent readings was reached with a feed rate in the neighborhood of 22 lb. per min. At rates above this value the film tended to be nonuniform and caused flooding of the tube. One of the reasons for this was the restricted space in the spray head for the delivery of such a high flow of liquid.

#### RESULTS

All measurements were made at one foot from the point of spray, and any velocities or thicknesses quoted, refer to measurements at this point.

Fig. 4 is the graphical expression of the measured film thicknesses plotted against feed rates. The film thickness increases steadily with feed rate until the tube is approximately one-quarter full. Above this value, a small increase in feed rate produces a large increase in film thickness which tends to a maximum (full bore conditions) at 34.9 lb. per min. As previously mentioned, measurements by the micrometer needle could not be made satisfactorily at rates higher than 22 lb. per min. This is indicated by the dotted portion of the curve.

The maximum average full bore velocity after one foot length was determined experimentally by the simple method of measuring the volume of liquid filling and falling freely with zero head through a one foot length of



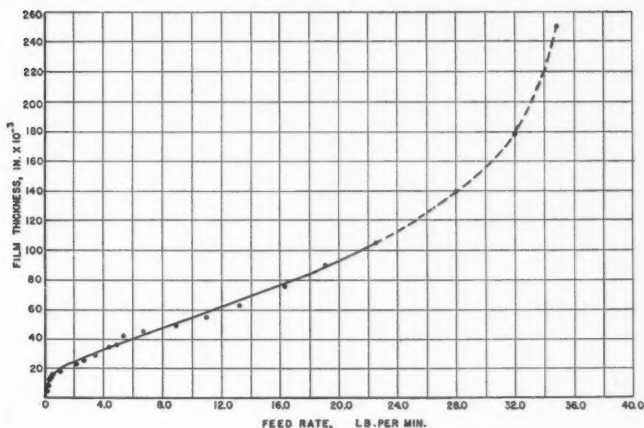


FIG. 4

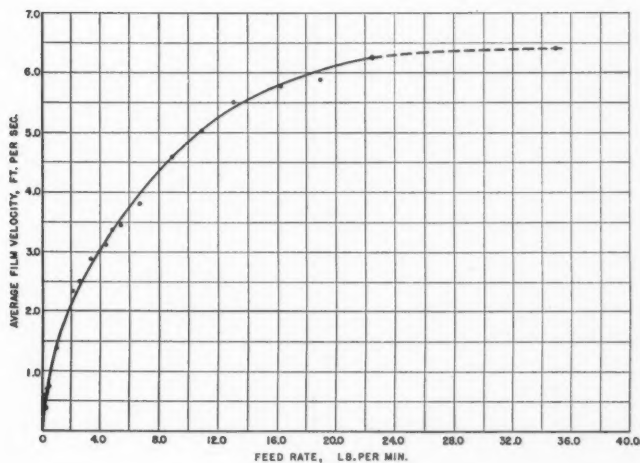


FIG. 5

copper pipe, 0.502 in. inside diameter. A value of 6.45 ft. per sec. was measured with a feed rate of 34.9 lb. per min. This corresponds to a Reynolds'

Number of 20,300 as calculated from the formula (2):  $Re = \frac{4W}{L_p \mu}$

where:  $Re$  = Reynolds' Number

$W$  = Rate of flow in lb., per sec.

$L_p$  = The wetted perimeter ( $\pi D$ ) in ft. and

$\mu$  = The viscosity of 5% sodium carbonate in  $\frac{\text{lb.}}{(\text{ft.}) - (\text{sec.})}$

The points intermediate between 22 lb. per min. and maximum full bore were calculated from the corresponding velocity values in the velocity-feed curve in Fig. 5.

The following calculation serves as a check on the experimentally determined maximum full bore velocity. Experiments show that the relation between the loss in head due to friction in pipes and the Reynolds' Number may be expressed for smooth circular pipes, such as brass, copper, and glass, by the expression (1):

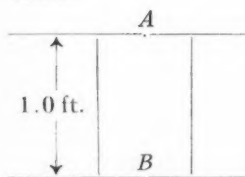
$$(1) \quad \frac{\Delta H_f D}{Lu^2} = 0.0000870 + \frac{0.00777}{(Re) 0.32}$$

where:  $\Delta H_f$  = loss in head due to friction, in ft.  
 $D$  = inside diameter of pipe in ft.  
 $L$  = length of pipe in ft.  
 $u$  = average velocity in ft. per sec.  
 $Re$  = Reynolds' Number

Applying Bernoulli's Theorem,  $\Delta H_f$  is determined as a function of the average velocity at point B;

$$(2) \quad X_A + \frac{u_A^2}{2g} + \frac{P_A}{\rho_A} - F + W = X_B + \frac{u_B^2}{2g} + \frac{P_B}{\rho_B}$$

where:



$X_A = 1.0$  ft. head  
 $F = \Delta H_f$   
 $u_B = u$  = average velocity at one foot, ft. per sec.  
 $P_A = P_B$ , and  $\rho_A = \rho_B$   
 $w = 0$   
 $u_A = 0$

Equation (2) becomes:

$$\Delta H_f = 1.0 - \frac{u^2}{2g}$$

Substituting this value of  $\Delta H_f$  in Equation (1) we obtain

$$\left(1.0 - \frac{u^2}{2g}\right) \left(\frac{D}{Lu^2}\right) = 0.0000870 + \frac{0.00777}{\left(\frac{Du}{\mu} \rho\right) 0.32}$$

where:

$\mu$  = viscosity of 5% sodium carbonate solution at 25° C. = 1.30 centipoises.  
 $D = 0.502$  in. = 0.0418 ft.  
 $L = 1.0$  ft.  
 $\rho$  = density of 5% sodium carbonate solution = 65.90 lb. per ft.<sup>3</sup>  
 $g = 32.2$  ft. per sec.<sup>2</sup>

Solving for  $u$ , we have:

$$0.01763 u^2 + 0.0140 u^{1.68} = 1.0, u = 6.30 \text{ ft. per sec.}$$

In this calculation the value of Reynolds' Number,  $\left(\frac{Du\rho}{\mu}\right)$  was  $3.150 u = 19,850$ .

It will be seen that calculated values for velocity and Reynolds' Number agree closely with those obtained experimentally.

The velocity-feed curve, Fig. 5, clearly indicates how the velocity increases rapidly with feed rate and then levels off to a maximum value in the neighborhood of 6.4 ft. per sec. Here as before, measurements could not be made successfully between the value of 22 lb. per min. and the maximum feed for full bore 34.9 lb. per min. The dotted portion, however, is fully justified since the line of the curve is clearly apparent.

Using the values of thickness measured, film velocities at the many feed rates were calculated. These values were employed to determine Reynolds' Number using the expression:

$$Re = \left(\frac{De u \rho}{\mu}\right)$$

where:  $De = 4m = 4 \left(t - \frac{t^2}{D}\right)$

and  $De$  = equivalent diameter in ft.  
 $m$  = hydraulic radius in ft.  
 $t$  = film thickness in ft.  
 $D$  = inside diameter of pipe in ft.

Viscosity values were those obtained by measurement in the Physical Chemistry Section of the Establishment and agreed closely with the values reported in the Critical Tables.

Fig. 6 shows the variation of Reynolds' Number with the measured velocities. For a given liquid and a given pipe, with full pipe flow, the Reynolds' Number - velocity graph is a straight line relationship since

$$Re = \frac{Du\rho}{\mu}, \text{ and } D, \rho, \text{ and } \mu \text{ are constants.}$$

The relationship is no longer linear when flow is filmwise (as shown in Fig. 6) since  $D$  and  $u$  are both variables.

By plotting the values of average film velocities against film thicknesses, we obtain the distribution of the average film velocity across the pipe, as shown in Fig. 7. For a film thickness equal to the radius of the pipe, i.e. full pipe flow, the value of the average velocity used was a mean value between the calculated and the experimental velocity. The curve resembles closely the general

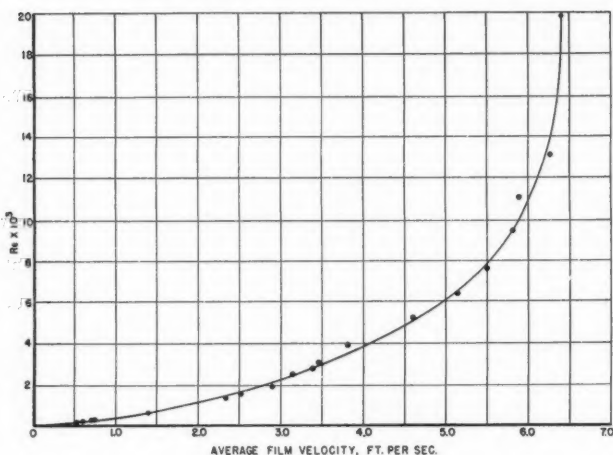
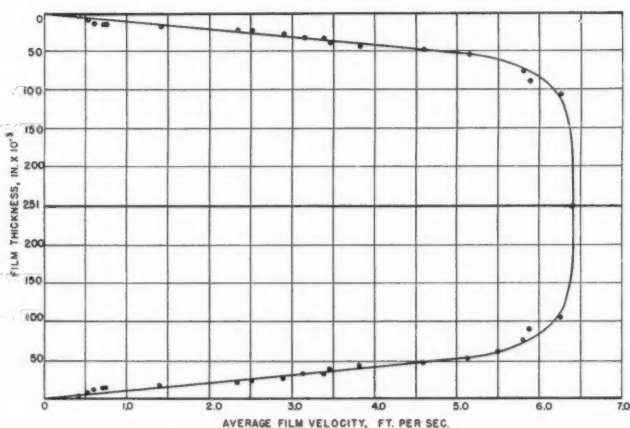


FIG. 6



DISTRIBUTION OF THE AVERAGE FLUID VELOCITY ACROSS THE TUBE

FIG. 7

trend for velocity distribution across a circular pipe under turbulent flow conditions. However, the slight difference is due chiefly to the fact that the velocity values employed are average velocities and not velocities determined at specific points across the pipe. These average velocities might be transformed into absolute velocities if one could apply the Stanton and Pannell (3) relationship, but this holds only for full bore flow in pipes. The only average velocity corresponding to full bore flow condition is the calculated and meas-

ured value of 6.4 ft. per sec. On applying Stanton and Pannell's relationship to this value we obtain the maximum velocity of 7.9 ft. per sec. in the middle of the tube. This value is in excellent agreement with calculated and theoretical values for this velocity.

#### CONCLUSIONS

The method of feed to the tube produced an even and steady film whose thickness could be measured easily and accurately over a wide range of feed rates. Results indicate that the method of film measurement is accurate and sensitive and can be applied *in situ* to many types of apparatus when the film medium is an electrolyte.

#### ACKNOWLEDGMENTS

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## TRACER STUDIES OF DIFFUSION IN SET PORTLAND CEMENT<sup>1</sup>

By J. W. T. SPINKS, H. W. BALDWIN, AND T. THORVALDSON

### ABSTRACT

A method has been developed for the study of diffusion processes in set Portland cement using radioactive ions;  $^{22}\text{Na}^+$ ,  $^{45}\text{Ca}^{++}$ ,  $^{131}\text{I}^-$  and  $^{35}\text{SO}_4^{--}$ . The diffusion constants for  $\text{SO}_4^{--}$ , determined at 4- and 12-week exposures, were of the same order for normal and sulphate resistant Portland cements. For the ions tested, anions had higher values for the diffusion coefficient,  $D$ , than cations.

### INTRODUCTION

It is well known that Portland cements are subject to attack by sulphate waters and that special sulphate resistant cements have been developed (6). In the past, sulphate resistance has been determined by a number of methods such as visual observation, strength change, change in length, and elastic modulus. When solutions of different sulphates such as those of sodium, calcium, and magnesium are used, differences in behavior are observed. Since diffusion processes might be expected to be of considerable importance in this problem, a study of diffusion processes in neat cement and mortar cylinders immersed in various sulphate solutions was undertaken. Solutions labeled with radioactive tracers were used, the underlying idea being that radioactive tracers would make it possible to follow a diffusing ion, such as calcium, in its passage through the cement even though the cement already contained a good deal of calcium. A purely chemical method of following the diffusion under these conditions would be difficult, if not impossible.

### METHOD

After trying various possibilities, the following method was adopted. A cylindrical specimen of neat cement or sand mortar, with sides coated with paraffin wax but with ends left bare, was immersed at constant temperature in a solution of the salt under investigation. One of the ions of the salt was labeled with a radioactive isotope:  $^{45}\text{Ca}$ ,  $^{35}\text{S}$ ,  $^{131}\text{I}$ , or  $^{22}\text{Na}$ . After a period of some weeks or months the specimen was removed from the solution and the radiation coming from the end measured with a Geiger counter (window thickness, 3.2 mgm. per sq. cm.; scale of 64 scaler). A thin layer of cement was removed by grinding and the activity again measured. For counting, the freshly ground surface was held in a fixed geometry with respect to the counter window and "edge effects" were eliminated by a diaphragm,  $\frac{3}{4}$  in. diameter, covering the outer rim of the surface (Fig. 1). By repeating this process, the extent of diffusion could be followed and diffusion constants calculated. The

<sup>1</sup> Manuscript received November 22, 1951.

Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask. Paper presented at the XIIth International Congress of Pure and Applied Chemistry, New York City, September 1951.



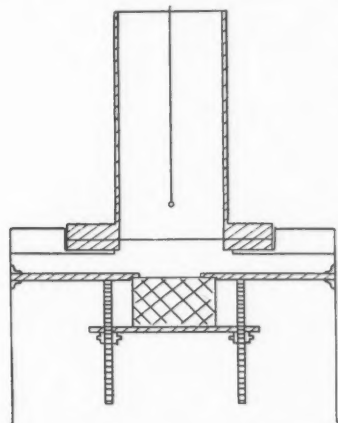


FIG. 1. Method of measuring radioactive cement cylinders under end window Geiger counter.

method is similar in principle to that used by Groh and Hevesy to measure self-diffusion in lead (3). The radiations emitted by the isotope have a certain range, say  $L_0$  cm. of material and the measured activity will, therefore, be due to electrons coming from within the layer of thickness,  $L_0$  (Fig. 2 and Table I).

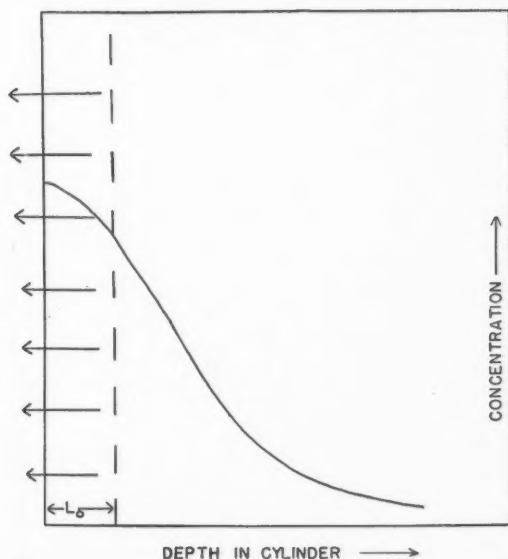


FIG. 2. Concentration gradient set up by diffusion of ions into briquettes.

TABLE I

	Range, mgm. per sq. cm. of Al	Thickness of cement, $L_0$ , mm., equiv. to range of $\beta$ particles
$^{35}\text{S}$	13.5	0.05
$^{45}\text{Ca}$	64	0.25
$^{22}\text{Na}$	215	0.85
$^{131}\text{I}$	155	0.6

Of course, not all the particles emitted within this layer will be measured, and, in fact, if we assume an exponential absorption of beta particles and a constant specific activity over the small thickness of material involved, the measured activity will be 10% of the true activity (4).

If we imagine the concentration of active material to fall off in a series of steps, of width  $L_0$ , the change in measured activity of the surface layer, as we cut off slices of thickness,  $L_0$ , will give a measure of the changing concentration of active material (Fig. 3). The situation is complicated somewhat in practice

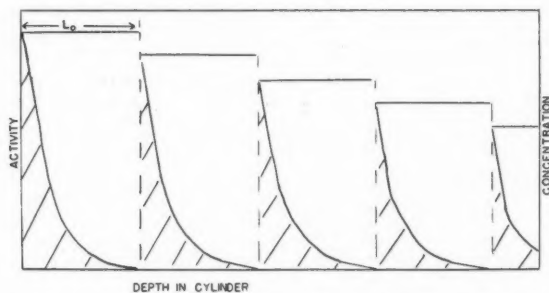


FIG. 3. Change of activity of cylinder as slices ground off assuming no change in concentration in depth  $L_0$ .

by the fact that there will be a concentration gradient set up by the diffusion process. However, if the distance of penetration of the radioactive ion is large compared to the range of the electrons in the material, we can easily show that the measured activity gradient will still give a reasonably accurate measure of the concentration gradient.

Consider two cases: (1) that there is no concentration change within the thickness equal to the range  $L_0$ , and (2) that there is a 50% drop in concentration within the depth,  $L_0$  (Fig. 4 (A), Curves 1 and 2). We can calculate the contribution to the measured activity by summing the activities of a series of thin slices from depth 0 to  $L_0$ , the activity from each slice being proportional to its specific activity times the fraction of radiation not absorbed by the overlying material (see Table II). This is plotted in Fig. 4 (B), Curve 2, together with the curve for no change in specific activity with depth in the slice, Fig. 4 (B), Curve 1. The total measured activity is proportional to

the area under the curve. The difference in areas under the two curves is about 4%. Since in most experiments the change in specific activity in a depth  $L_0$  is less than 10%, the error introduced by assuming no change in concentration is less than 1%, which is much better than the accuracy of other parts of the experiment.

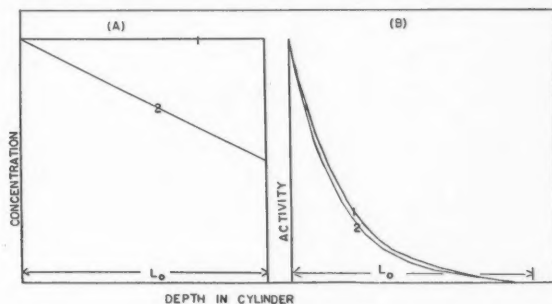


FIG. 4. Effect of change in concentration on radiation coming from slice of thickness  $L_0$ .

Thus, the activity gradient, as measured by the radiation coming from the end of the specimen, gives a reasonably accurate measure of the concentration gradient for the present experiments.

Obviously, the thickness of the slice ground off need not necessarily be  $L_0$ . In a general way, the thinner the slice, the more accurately will the concentration gradient curve be established. The amount removed by each grinding was about 0.1 mm. in the present experiments and was determined by measuring the thickness after each grinding (average of nine readings). Distances of penetration for times of a month or more are usually several millimeters and thus the requirements of Fig. 4 are met very well for  $^{45}\text{Ca}$  and  $^{35}\text{S}$ , and reasonable results will be obtained even for isotopes such as  $^{22}\text{Na}$  or  $^{131}\text{I}$  (2).

TABLE II  
ESTIMATION OF RADIATION ESCAPING FROM END OF CYLINDER WITH NONUNIFORM  
CONCENTRATION OF RADIOACTIVE ION

Depth of thin slice as fraction of $L_0$	Fraction of activity measured	Relative specific activity of the thin slice for 50% change in conc. in distance $L_0$	Measured activity (Col. 2 $\times$ Col. 3) <sup>1</sup>
0.0	1.0	1.0	1.0
0.1	0.63	0.95	0.59
0.2	0.4	0.9	0.36
0.3	0.25	0.85	0.21
0.4	0.15	0.8	0.12
0.5	0.095	0.75	0.07
0.6	0.062	0.7	0.042
0.7	0.04	0.65	0.026
0.8	0.025	0.6	0.015
0.9	0.015	0.55	0.008
1.0	0.01	0.5	0.005

## MATERIALS

The cement cylinders were about 1 in. in diameter and 2 in. in length. They consisted of either a neat cement or a mortar composed of one part of cement to two parts of standard Ottawa sand (20–30 mesh). Two commercial cements were used, one being a "normal" cement (Type I by A.S.T.M. Standards) and the other a sulphate resisting cement (Type V by A.S.T.M. Standards).

$^{35}\text{S}$  (as sulphate),  $^{45}\text{Ca}$  (as carbonate), and  $^{131}\text{I}$  (as iodide) were obtained from the National Research Council, Chalk River, Ont.; while  $^{22}\text{Na}$  (as chloride) was obtained from the United States Atomic Energy Commission. Their half lives and absorption half thicknesses agreed with the published values. Solutions of 0.15 *M* sodium sulphate, 0.15 *M* sodium iodide, and saturated calcium sulphate were prepared, labeled with  $^{22}\text{Na}$ ,  $^{35}\text{S}$ ,  $^{131}\text{I}$ , and  $^{45}\text{Ca}$ . Radioactivity of the solutions was approximately  $10^4$  counts per minute per milliliter.

## RESULTS

The above method gives a series of values of the activity in layers of thickness,  $L_0$ , at increasing depths from the surface, e.g., Table III (a).

TABLE III  
EXPERIMENTAL DATA FOR A TYPICAL DIFFUSION EXPERIMENT  
NEAT CEMENT EXPOSED TO SATURATED  $\text{Ca}^{35}\text{SO}_4$  SOLUTION FOR 4 WEEKS

(a) Experimental data		(b) Calculation of $\beta$			
Depth, mm.	Activity, reg. per min.	$x$ , cm.	$c$	$\frac{c}{c_0}$	$\beta$
0.00	17.73	0.00	17.7	1.00	0.00
0.09	14.17	0.01	12.7	0.718	0.26
0.25	44.04	0.02	6.2	0.350	0.66
0.46	0.81	0.03	2.9	0.164	0.99
0.63	0.18	0.04	1.2	0.0678	1.29
0.81	0.03	0.05	0.55	0.0311	1.52
		0.06	0.19	0.0107	1.81

By solving Fick's general law of diffusion for the case of diffusion into a semi-infinite solid, and putting in the limits applying to our experiments, namely  $c = c_0$  at  $x = 0$ , for all values of  $t$ :

$$1 - \frac{c}{c_0} = \frac{2}{\sqrt{\pi}} \int_0^\beta e^{-y^2} dy,$$

where  $c$  is the concentration of the diffusing ion at a depth,  $x$ , and a time,  $t$ , (1 (see particularly pp. 12, 97), 7).  $\beta = \frac{x}{2} \sqrt{Dt}$  and  $D$  is the diffusion coefficient;  $c$  is proportional to the activity observed at depth,  $x$ , and time,  $t$ . The value of  $\beta$  for which the probability integral  $\frac{2}{\sqrt{\pi}} \int_0^\beta e^{-y^2} dy$  equals  $1 - \frac{c}{c_0}$

may be read from tables (5). For a given value of  $t$  and assuming  $D$  is constant,  $\frac{\beta}{x} = \frac{1}{2}\sqrt{Dt} = \text{a constant}$  and a plot of  $\beta$  versus  $x$  should give a straight line. Figs. 5 and 6 illustrate the type of plot obtained from the data in Table III (a) and (b). The slope of the line in Fig. 6 gives the average value of  $\frac{\beta}{x}$ . The diffusion coefficient is obtained from  $D = \frac{1}{4}t\left(\frac{x}{\beta}\right)^2$ .

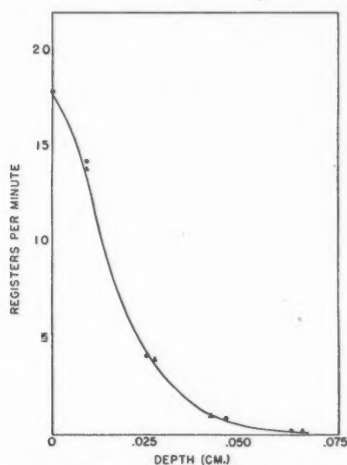


FIG. 5. Plot of activity versus depth in cylinder; neat cement in saturated calcium sulphate solution, four weeks. ●, data in Table IIIa; ▲, corresponding points for other end of cylinder (data not presented in Table IIIa).

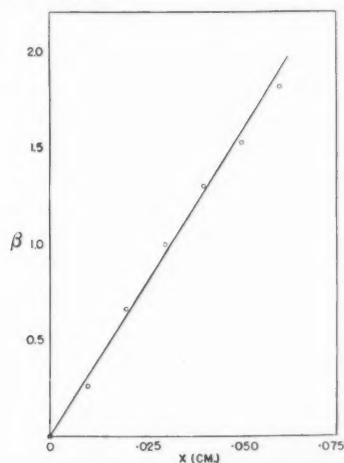


FIG. 6. Plot of  $\beta$  versus  $x$ ; neat cement in saturated calcium sulphate solution, four weeks (Table IIIb).

## CALCULATION OF CONCENTRATION OF LABELED ION IN SPECIMENS

In the foregoing,  $D$  values are calculated from the change in activity with no mention of actual amounts of sulphate which have diffused into the specimen. This can be determined if specimens containing known amounts of radioisotope are prepared as standards, with which the activity of test specimens can be compared. For example, 0.15  $M$  sodium sulphate was prepared with an activity of 0.094 mc. of  $^{35}\text{S}$  per liter, i.e., a specific activity of 6.52  $\mu\text{c.}$  per gm. sulphate. A standard neat cement specimen weighing 36.6 gm. was prepared in which 7.13  $\mu\text{c.}$   $^{35}\text{S}$  had been uniformly incorporated. The "activity" of an end, measured in the usual way, was 14.09 registers per minute. The density of the neat cement was 2.3 and thus 1 register per minute  $\equiv$  4.86 mgm.  $\text{SO}_4^-$  per  $\text{cm.}^3$  neat cement.

The total amount of sulphate which has passed through 1  $\text{cm.}^2$  of the surface would be obtained by graphical integration in the plot of activity of surface (in registers per minute) versus the depth in centimeters (the "depth" is the distance of the plane, at which activity measurements are made, from the original exposed surface). Actually, in this example, milligrams of sulphate which have penetrated 1  $\text{cm.}^2$  of surface equals 4.86 times the area under the curve. This enables one to calculate the amount of sulphate entering the two ends of the specimen. In a typical experiment, in which the specimen was exposed to 50 ml. 0.15  $M$  sodium sulphate for one month, 20 mgm.  $\text{SO}_4^-$  entered the specimen. This would reduce the concentration to 0.145  $M$  and this checked satisfactorily with experiment, 0.143  $M$ . Incidentally, these measurements indicate that the concentration of the solution remained essentially unchanged during the experiment.

Additional experiments showed that the activity measured from the end was directly proportional to the amount of activity used in preparing the standard specimen and that the activity was essentially uniformly distributed throughout the standard specimen.

## REPRODUCIBILITY OF RESULTS

In an attempt to avoid unwanted surface effects, 2 in. long cement cylinders were cut, with water cooling with a diamond saw, into  $\frac{1}{2}$  in. long pieces. In one set of experiments the surface received no further treatment; in another set, the somewhat uneven surface left by the saw was ground down smooth.  $D$  values for these surfaces are recorded in Table IV.

The excellent agreement for the cut and ground surfaces indicated in Table IV is probably fortuitous, but it indicates that this method will give reasonably reproducible results. Surfaces prepared in this way were used in all the work reported here.

Results obtained of the foregoing method for a number of ions on a typical normal cement and a sulphate resistant cement are summarized in Tables V and VI.



TABLE IV

REPRODUCIBILITY OF  $D$  VALUES FOR CUT AND GROUND SURFACES $D_{SO_4^{2-}}$  for neat cement in 0.15  $M$  sodium sulphate, 28 days, surface formed by diamond saw

No further treatment	Surface ground smooth
$2.19 \times 10^{-10}$ cm. <sup>2</sup> per sec.	$2.07 \times 10^{-10}$ cm. <sup>2</sup> per sec.
$3.45 \times 10^{-10}$ cm. <sup>2</sup> per sec.	$2.07 \times 10^{-10}$ cm. <sup>2</sup> per sec.

TABLE V

COMPARISON OF  $D$  FOR TYPE I (NORMAL PORTLAND CEMENT) AND TYPE V (SULPHATE RESISTING PORTLAND CEMENT) IN 0.15  $M$  Na<sub>2</sub><sup>35</sup>SO<sub>4</sub> IN SATURATED Ca<sup>35</sup>SO<sub>4</sub>  
(APPROX. 0.015  $M$ ) AT ROOM TEMPERATURE $D_{SO_4^{2-}} \times 10^{10}$ , cm.<sup>2</sup>, sec.<sup>-1</sup> (21 to 22° C.)

Time of exposure	Exposed to:							
	0.15 M Na <sub>2</sub> SO <sub>4</sub>				Saturated CaSO <sub>4</sub> solution			
	Type of cement							
	Type I		Type V		Type I		Type V	
	Mix							
	Neat	1:2 Mortar	Neat	1:2 Mortar	Neat	1:2 Mortar	Neat	1:2 Mortar
4 weeks	1.3	8.9	1.4	9.4	1.5	8.5	2.6	9.5
12 weeks	0.6	5.4	0.7	5.6	0.9	5.3	0.9	2.7

TABLE VI

RELATIVE VALUES OF  $D$  FOR POSITIVE AND NEGATIVE IONS FOR NEAT CEMENT AND MORTARS EXPOSED TO 0.15  $M$  SOLUTIONS (AND TO SATURATED CaSO<sub>4</sub>) $D \times 10^{10}$ , cm.<sup>2</sup>, sec.<sup>-1</sup> (21 to 22° C.)

Time of exposure of specimens	$D_{Na^+}$ in 0.15 $M$ Na <sub>2</sub> SO <sub>4</sub> 1:2 mortar	$D_{SO_4^{2-}}$ in 0.15 $M$ Na <sub>2</sub> SO <sub>4</sub> 1:2 mortar	$D_{I^-}$ in 0.15 $M$ NaI 1:2 mortar	$D_{Ca^{++}}$ in sat. CaSO <sub>4</sub>		$D_{SO_4^{2-}}$ in sat. CaSO <sub>4</sub>	
				Neat	1:2 mortar	Neat	1:2 mortar
4 weeks	3.0	6.1	130	0.10	2.8	1.5	8.5
12 weeks	—	—	—	0.25	0.21	0.9	5.3

## DISCUSSION

Some tentative conclusions may be drawn from Tables V and VI.

(a) The diffusion constants for  $\text{SO}_4^{2-}$ , determined at 4-week exposure and at 12-week exposure for a Type I and a Type V Portland cement, are of the same order. The difference in the resistance of these two types of cement to sulphate action is thus probably not due to variation in the rate of diffusion of the sulphate into the set cement or mortar.

(b) For the above experiments, anions have higher  $D$  values than cations.

(c) In general,  $D$  values decrease with time of exposure to the solution. The drop between the 4-week and 12-week exposures is large; between 12-week and 24-week values (not reported here) is much smaller.

The foregoing results indicate that diffusion experiments in cement, using radioactive tracers, can yield interesting and worthwhile results. It is hoped that the variation in  $D$  with a number of factors, such as nature of the diffusing ion, pretreatment of the cement specimen, composition of the specimen, etc., will eventually throw some light on the general problem of cement deterioration.

## ACKNOWLEDGMENT

We are grateful to the National Research Council of Canada for continued financial support.

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## THE OXIDATION, DECOMPOSITION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

### XIX. OPTIMUM TIMING OF COMPRESSION OR SPARK IGNITION AS DETERMINED BY ADJUSTMENT OF COMPRESSION RATIO; ACETALDEHYDE AND DIETHYL ETHER AS ENGINE FUELS<sup>1</sup>

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#### ABSTRACT

Acetaldehyde and diethyl ether were used as the fuels for a C.F.R. carburetor type engine run in the cool conditions required to ensure the presence in the charge of liquid drops during compression. Charge density was subnormal and compression ratio was then always adjustable to the value required for maximum power output (the optimum value), without inducing knock of intolerable intensity when using rich mixtures. The spark plugs of the engine were replaced by blind plugs for experiments with compression ignition and both fuels were used with mixture strengths varying from 75% weak, B.H.P. then being zero, to 140% rich. The graphs relating optimum C.R. to mixture strength are of a W form with two minimum values of optimum C.R. and an intermediate maximum value. Spark ignition was not effective with mixtures leaner than 40% weak or more than 80% rich. A relatively low engine speed of 400 r.p.m., and the presence of liquid drops in the charge during compression, provided conditions suitable for liquid phase cracking and the compression ignition obtained in the conditions of the experiments is attributed to the effect of nuclei formed accordingly. The experimental results afford evidence of thermal efficiency being affected adversely by the loss during compression of the heat required by the endothermic cracking reaction which produces the nuclei required for compression ignition.

#### INTRODUCTION

The experiments with acetaldehyde and diethyl ether described in Part XVIII (5) were made with a cool engine, wet carburetion, and normal charge density. Spark ignition was fixed at 10° advance and on adjusting compression ratio to obtain a standard knock intensity, as indicated by a bouncing pin meter, the engine would run with the spark switched off and with no appreciable change of power output.

The term "compression ratio" will be replaced hereafter by the initial letters C.R.

When using a particular mixture strength and continuously increasing C.R., power output increased to a maximum value and then decreased. An optimum C.R. was thus obtainable at which compression ignition timing was such that maximum combustion pressure probably occurred at the suitable piston position which was shown by indicator diagrams to be approximately 10° to 12° after top dead center, for liquid fuels.

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The optimum C.R. could be determined in the manner described for extremely weak mixtures only. Knock intensity became intolerably severe when C.R. was increased to the optimum value for relatively rich mixtures. Knock intensity decreases with a decrease of charge density and the experiments of this Part were therefore carried out with charge density reduced sufficiently to allow the use of optimum C.R. regardless of mixture strength. Mixtures varying from 75% weak to over 300% rich were used for the experiments but the results obtained with mixtures more than 140% rich are not presently described. Knock intensity varied accordingly but was never intolerably severe.

The bouncing pin was not required in the circumstances and was replaced by a blank steel plug.

Two sets of experiments with acetaldehyde and diethyl ether are described in this Part: one with the three spark plugs of the engine replaced by mild steel blanks, "blind plugs"; the other with one spark plug and ignition timing fixed at 10° advance in order to reduce the number of variables. C.R. was always adjusted for maximum power output which occurs necessarily with optimum ignition timing.

No difficulty was experienced in starting from cold when using either fuel, even when blind plugs replaced the spark plugs, if C.R. were set at approximately half a ratio higher than the optimum value.

#### ARRANGEMENTS MADE TO PROVIDE THE CONDITIONS OF EXPERIMENT *Wet Carburetion*

Vaporization of the fuel in the carburetor was restricted by maintaining the air supply at the relatively low temperature of 50° F. and by removing the diffuser. The standard C.F.R. mixture heater was removed, allowing attachment of the carburetor directly to the engine head. The cooling water entered the cylinder jacket at 95° F. and the rise in temperature was restricted to 5° F. by automatic thermostatic control, as described in Appendix (b) Part XIII (6). These arrangements ensured the presence of a wet mixture at the start of compression and vaporization may not have been completed during compression. Completion would depend on mixture strength.

#### *Air Conditioning*

It is necessary in the operating conditions required for wet carburetion that relatively dry air be used in order to avoid the formation of ice in the carburetor throat. Air sufficiently dry was obtained for experiments described in earlier Parts by drawing the supply in mid-winter from outside the laboratory building. Air conditioning equipment provided subsequently made possible the continuation of cool engine experiments irrespective of weather conditions. A lagged 45 imperial gallon oil drum fitted internally with three concentric spiral cooling coils of copper tubing, and with suitable air baffles, was used as an addition to the air metering arrangement described in Appendix (c) of Part XIII (6, pp. 154-155) and incidentally increased the air oscillation damping

capacity. A  $\frac{1}{2}$  h.p. Freon-12 air cooled condensing unit and three Alco T.K.O.F. Freon expansion valves, one for each cooling coil, sufficed to maintain an air temperature of approximately 5° F. in the cooling drum while air from the laboratory atmosphere was drawn through it at the rate required by the engine. The cooling coils were always defrosted on completion of a set of experiments. The temperature of the air leaving the drum was raised to 50° F. by an electric strip heater before entering the carburetor. The relative humidity was then 25% approximately and ice was not formed in the carburetor.

### *The Engine*

A C.F.R.-F. 2. engine was used for the experiments. It was fitted with balancing pistons and three spark plugs. It was similar otherwise to the C.F.R. knock testing engine used for experiments described in preceding Parts. The standard shrouded inlet valve was replaced by one of the common variety—a spare exhaust valve. The spark plugs and the bouncing pin were replaced by mild steel blanks, "blind plugs". An engine speed of 400 r.p.m. was used for the experiments.

### *Carburetor for Subnormal Charge Density*

The standard C.F.R. carburetor was modified to provide the subnormal charge density required for the experiments. Thus the diffuser was removed and the expanding nozzle replaced by a choke tube as illustrated by Fig. 5. The choke tube was curved to discharge the wet fuel-air mixture into the engine head well containing the inlet valve. This arrangement led to greater regularity of engine running than when an expanding nozzle was used and the liquid drops in the fuel-air mixture tended to adhere to the rough surfaces in the induction passage in the engine head. The 9/16 in. throat diameter of the venturi in the standard carburetor is overlarge when the engine speed is reduced from the usual 900 r.p.m. to the 400 r.p.m. used for the experiments of this Part and the reduction in charge density due to the use of choke tubes of relatively small diameter was consequently less than would otherwise have been expected. Thus even with a choke tube of 0.25 in. internal diameter the charge densities, which vary with the boiling points and heats of vaporization of the fuels used, were 62% and 67% of the normal value for diethyl ether and acetaldehyde respectively, at the engine speed of the experiments; the normal value being that obtained when the standard C.F.R. carburetor is used, and volumetric efficiency 85%, as determined by measurement of rate of air supply.

### *Metering of the Fuel and Air*

The standard C.F.R. method of controlling the fuel supply to the engine depends on varying the "head" on a small orifice in the fuel passage leading to the carburetor. Orifices less than 0.010 in. in diameter were required at an engine speed of 400 r.p.m. when extremely weak fuel-air mixtures were used. The flow through the orifices, as used with the C.F.R. method of control, was then unstable. It was found that steady flow at the extremely small

rates required was obtainable by using a fine adjustment needle valve; fuel supply being from a constant head. The flow was metered by the weighing method. The air supply to the engine was metered by the orifice method described in Appendix (c) Part XIII (6). The acetaldehyde and diethyl ether used as engine fuels were as described in Part XVIII (5).

#### *Spark Ignition System*

The standard C.F.R. spark ignition system was found to be unsatisfactory when weak mixtures of gaseous fuels were used at relatively high compression ratios. It was replaced by a special Auto-Lite system suggested by Mr. Chester Cipriani (6, pp. 152-153). The system has been used since for all experiments for which spark ignition was required. Sparks over an inch in length in air at atmospheric pressure were obtainable with the system as used, and spark ignition was obtained in the engine when using fuel gases at a C.R. of 20:1, with normal charge density.

#### *Measurement of Brake and Indicated Horsepower*

Brake horsepower was measured by a swinging field direct connected electric dynamometer and the indicated horsepower obtained by adding the lost horsepower as determined by the motoring method. The horsepower lost in friction was reduced as far as possible by lubricating the engine with a low viscosity oil, S.A.E. 10, and maintaining the temperature of the oil in the crank case at 120° F. Measurements of lost horsepower, made later than 12 sec. after firing ceased, were not recorded.

#### TEMPERATURE CONDITIONS FOR COOL ENGINE EXPERIMENTS

It was possible in consequence of the use of refrigeration to maintain the air supply to the carburetor of the C.F.R. engine at an invariable and relatively low temperature. 50° F. was selected as not being significantly different from the temperatures used for the cool engine experiments described earlier, which were dependent on variable winter air temperatures. It is probable that the use of a relatively low air supply temperature, in conjunction with the carburetor attached directly to the engine head, ensured that even a weak mixture entering the cylinder contained some proportion of the fuel as droplets. The temperature of such a mixture would vary with the nature of the fuel and, in any event, it is indeterminate and measurement was not attempted.

The temperature of the cooling water entering the cylinder jacket was maintained at 85° F. for the cool engine experiments with benzene (3), pentane (4), and acetaldehyde (5). A lower temperature of 75° F. was used for experiments with ether (5) mainly because that substance is reputed to "detonate more readily than any other," (8, p. 85). The flow of cooling water was in all instances regulated automatically for a rise of 5° F. in the jackets. Exceptionally low jacket coolant temperatures were found to be unnecessary for experiments with ether and in order to reduce piston friction and thus increase the accuracy of measurement of indicated thermal efficiency, an inlet temperature of 95° F. was adopted for a new series of nuclear ignition experiments of which those of this Part are the first to be described.



The relation between the coolant temperature and that of the *mean* temperatures of surfaces in the cylinder has been determined by others for some conditions of engine operation. There is, however, no information available concerning the *true* surface temperatures which must undergo extreme cyclic changes and be an important factor in respect of the surface oxidation reactions which in turn influence fuel performance.

## EXPERIMENTAL RESULTS

### Acetaldehyde

The *B* graphs of Fig. 1 exhibit experimental results obtained when the spark plugs and bouncing pin were replaced by blind plugs, the charge density reduced to 67% of normal and the compression ratio always adjusted to the optimum value. The correct air to fuel ratio for acetaldehyde is 7.84:1 by weight. Mixtures varying from 75% weak to 140% rich were used. *Brake horsepower* was zero with a mixture 75% weak. The air to fuel ratio was then 31.4:1, by weight.

The optimum C.R., lower *B* graph, Fig. 1, decreased from 11.9 to 8.1 as mixture strength was increased from 75% weak to 44% weak but on further

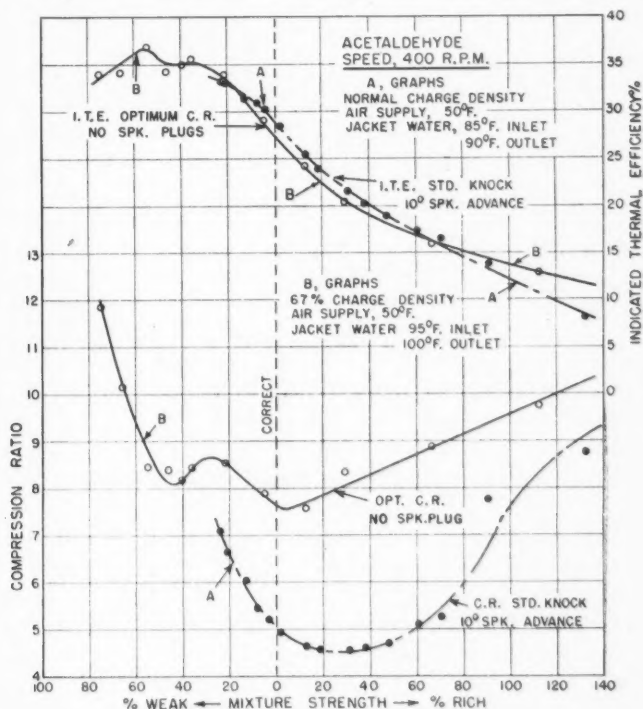


FIG. 1. Acetaldehyde. Results obtained with compression ignition, blind plugs, and reduced charge density compared with those obtained with spark ignition, standard knock intensity, and normal charge density.

increasing mixture strength to 28% weak, optimum C.R. increased to 8.7, and then decreased to a minimum of 7.5 on further increasing mixture strength to be 5% rich. Thereafter the increase of optimum C.R. with increase of mixture strength was nearly linear. Thus in the conditions of the experiment there were two minimum but unequal values for the optimum C.R. The first, occurring with the mixture 45% weak, is reflected in the graph for indicated thermal efficiency. There is no inflection in the graph in respect of the second minimum.

Combustion was silent when extremely weak mixtures were used but became audible as mixture strength was increased. Light knock occurred with a mixture 40% weak. Knock intensity continued to increase with increase of mixture strength to become medium heavy and somewhat irregular for the correct mixture. It became irregularly heavy and was accompanied by some missing as the mixture strength was increased to be 140% rich. The observations of knock intensity were made when using the optimum C.R.

It is of interest to compare the experimental results described above with those obtained when using normal charge density and always adjusting C.R. for a standard knock intensity as indicated by the bouncing pin meter; circumstances in which the engine would run with or without spark ignition. The broken line, *A* graphs of Fig. 1, have been reproduced accordingly from Part XVIII (5).

It will be seen by reference to Graphs *A* that the earlier experiment was discontinued when the mixture was 25% weak. Both spark and compression ignition were then ineffective and knock exceeded that adopted as a standard intensity as indicated by the knock meter, on attempting to continue with compression ignition by raising the C.R. It was indicated, however, that compression ignition might remain effective as the mixture was progressively weakened while spark ignition would not. This difference between compression and spark ignition was not confirmed until charge density was reduced in order to mitigate the severity of the knocking combustion which occurred with mixtures even as rich as 25% weak. It appears, however, that Graph *A* would have intersected Graph *B* if it had been practicable to carry on with compression ignition after spark ignition had become ineffective, without reducing charge density.

A second significant feature displayed by the experimental results given by the *A* and *B* graphs of Fig. 1 is that the higher C.R. required for optimum compression ignition timing yielded a somewhat lower value for indicated thermal efficiency than was obtained when ignition was with or without spark ignition and C.R. adjusted for the lower value then required for a standard knock intensity. Relative values are given in Table I for mixture strengths in the range commonly used.

It is shown by the data of Table I that with a 15% weak mixture equal values were obtained for thermal efficiency although C.R. was 6.1, *A* graph, and 8.2, *B* graph, whereas according to the ordinary rules of calculation there

should have been a 10% difference. A decrease in thermal efficiency is shown for the correct mixture on raising the C.R. from 5 to 7.6, a change which should have given a percentage *increase* of 17. The anomalous effect is even greater for the 40% rich mixture for which, on increasing C.R. from 4.6 to 8.3, a decrease in thermal efficiency of 5% was observed, instead of a calculated *increase* of 22%.

TABLE I  
COMPRESSION RATIO AND INDICATED THERMAL EFFICIENCY

Mixture	A Graphs		B Graphs	
	Standard knock intensity normal charge density. With or without spark ignition		Optimum compression ignition timing, 67% charge density blind plugs	
	C.R.	I.T.E., %	C.R.	I.T.E., %
15% weak	6.1	32	8.2	32
Correct	5.0	29	7.6	27½
40% rich	4.6	20	8.3	19

#### Diethyl Ether

The *B* graphs of Fig. 2 exhibit results of experiments made with ether when the spark plugs and the bouncing pin were replaced by blind plugs, the charge density reduced to 62% of normal, and C.R. always adjusted to the optimum value. The correct air to fuel ratio for diethyl ether is 11.2:1 by weight. Mixtures varying from 75% weak to 140% were used. Brake horsepower was zero with a mixture 75% weak. The air to fuel ratio was then 44.8:1.

The broken line *A* graphs of the figure are reproduced from Part XVIII (5) and exhibit experimental results obtained when using normal charge density and always adjusting C.R. for a standard knock intensity as indicated by the bouncing pin meter, circumstances in which the engine ran with or without spark ignition.

A comparison of Graphs *A* and *B* shows that the inflection in Graph *A* which in the earlier experiment was considered as possibly due to experimental irregularity (5, p. 385) did in fact indicate a real effect which, when using the new method of experiment, became the first of two minimum and equal values of the optimum C.R.; the corresponding mixture strengths being 40% weak and 25% rich respectively. The intermediate maximum value of the optimum C.R. occurred with a mixture 10% weak and was as shown by Graph *B*, 1.75 C.R. higher than the minimum values. A nearly symmetrical *W* form is imparted accordingly to the graph for optimum C.R. over the mixture range 65% weak to 80% rich.

It will be noted that the *A* and *B* graphs, Fig. 2, for the relation between compression ratio and mixture strength, intersect when the mixture is 25% weak and the compression ratio 6.0. On the rich side of the intersection,

thermal efficiency decreases with increase of C.R. This anomalous effect is similar, though somewhat smaller than was obtained when using acetaldehyde as the engine fuel. On the weak side, a higher thermal efficiency corresponds with the use of a higher C.R. but the relation is not in accordance with known factors. Graph *B* of Fig. 2, for I.T.E., would be of more nearly conventional form if it were as shown by the dotted line. Too much reliance cannot be placed on the observation made with the mixture 70% weak.

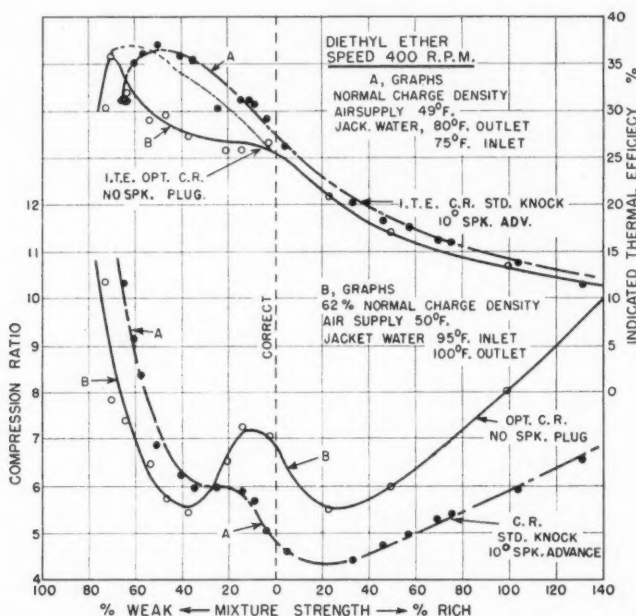


FIG. 2. Diethyl ether. Results obtained with compression ignition, blind plugs, and reduced charge density compared with those obtained with spark ignition, standard knock intensity, and normal charge density.

Combustion was silent when extremely weak mixtures were used. Light knock developed as mixture strength was increased to 40% weak. It continued to increase with increase of mixture strength and to become medium heavy for mixtures approximately correct. The intensity became somewhat variable as between medium heavy, and heavy, with mixtures ranging from correct to 140% rich. Misfiring occurred occasionally. Knock intensity characteristics were, as nearly as could be judged by ear, similar to those observed during the experiments with acetaldehyde although that substance required higher values of the C.R. for optimum ignition timing. The running of the engine with ether as the fuel was noticeably smoother than when acetaldehyde was used.

*Acetaldehyde. Results of Experiments with Spark Ignition Compared with Results Obtained with Compression Ignition; 67% of Normal Charge Density*

It was shown by experiments described in Part XVIII (5), and reviewed earlier in this Part, that ignition of acetaldehyde-air mixture varying from 25% weak to 140% rich would occur with or without spark ignition if C.R. were adjusted for a standard knock intensity. The experiments were made with normal charge density, and spark ignition was always set at 10° advance. Spark ignition failed when mixture strength was leaner than 25% weak. Compression ignition also failed if C.R. were restricted to the value for standard knock intensity.

The results of reducing the charge density to 67% of normal and using the optimum C.R. while retaining spark ignition are exhibited by the C graphs of Fig. 3. Spark ignition was ineffective when the mixture was leaner than 40% weak, but it was possible to continue into weaker mixtures with ignition by compression, always using the optimum C.R., until the mixture became 75% weak and power output zero.

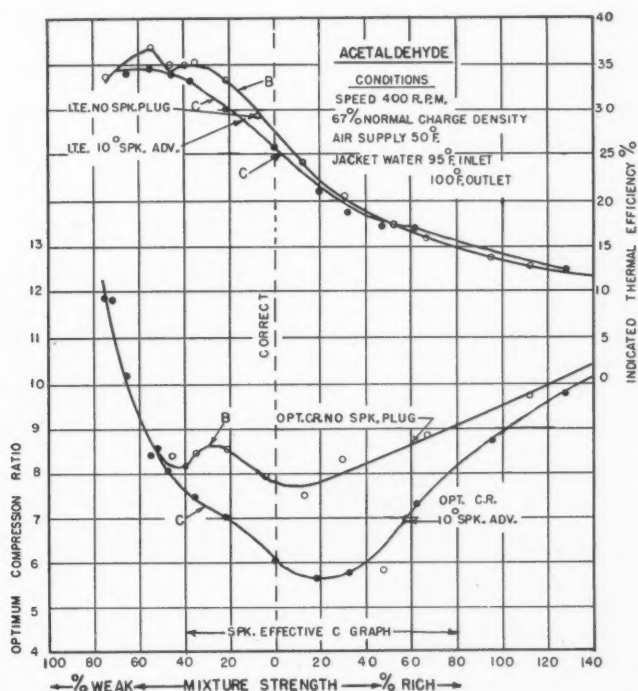


FIG. 3. Acetaldehyde. Results obtained with and without spark ignition and in both cases using optimum compression ratio, reduced charge density, and same temperature conditions.

Combustion was silent with extremely weak mixtures. Knock became audible and very light on increasing mixture strength to 40% weak and became light only, even on increasing mixture strength to 80% rich. It became medium heavy for a mixture 140% rich.

The *B* graphs of Fig. 3 are reproduced from Fig. 1, and exhibit experimental results obtained with charge density 67% of normal, and with blind plugs instead of a spark plug; the optimum C.R. for compression ignition always being used. Graphs *B* and *C* thus represent experimental results obtained in like conditions of charge density and engine and air supply temperatures.

Comparing the two graphs, giving the relation between optimum C.R. and mixture strength, it will be seen that for mixtures leaner than 40% weak, the experimental points for both sets of experiments fall on a single line as would be expected in view of spark ignition having become ineffective. It also became ineffective, as already mentioned, when mixture strength was more than 80% rich but the graphs do not then coincide. It is evident that the spark plug introduced an igniting effect not due to the spark.

It is of interest to compare the relation between thermal efficiency and C.R. observed when blind plugs were used with the similar relation observed when ignition was by spark; C.R. being adjusted for optimum ignition timing in both cases. The comparison is made only for mixtures increasing in richness from 40% weak, in part because of spark ignition being ineffective with weaker mixtures. Relevant data from the originals of the graphs of Fig. 3 are tabulated below.

TABLE II  
RELATIVE EFFECTS OF COMPRESSION AND SPARK IGNITION ON INDICATED THERMAL EFFICIENCY (I.T.E.) WITH ACETALDEHYDE AS ENGINE FUEL, SAME CHARGE DENSITY BOTH CASES

Mixture	Opt. C.R. (spark)	Opt. C.R. (blind plugs)	I.T.E. (spark), %	I.T.E. (blind plugs), %	% Increase I.T.E.	Calculated inc., %
40% weak	7.7	8.2	33½	35	4.5	2.0
20% weak	7.0	8.5	30	33	10.0	6.3
Correct	6.0	7.8	25½	27½	7.8	9.3
20% rich	5.6	7.8	21	22½	7.2	12.8
40% rich	5.9	8.2	18	19	5.5	12.0

The compression ignition obtained when using blind plugs appears to yield an increase in thermal efficiency for mixtures weaker than correct and a decrease for correct and richer mixtures.

*Diethyl Ether. Results of Experiments with Spark Ignition Compared with Results Obtained with Compression Ignition; 62% of Normal Charge Density*

The *B* and *C* graphs, Fig. 4, exhibit experimental results obtained when charge density was 62% of normal. The *B* graphs are reproduced from Fig. 2 and give results obtained without spark plugs and with the optimum



C.R. for compression ignition. The *C* graphs give results obtained with one spark plug, spark timing being set  $10^\circ$  advance, and the C.R. adjusted for maximum power.

Comparing the *B* and *C* graphs, giving the relation between optimum C.R. and mixture strength, it will be seen that the characteristics are in general similar to those observed when acetaldehyde was used as the fuel for the

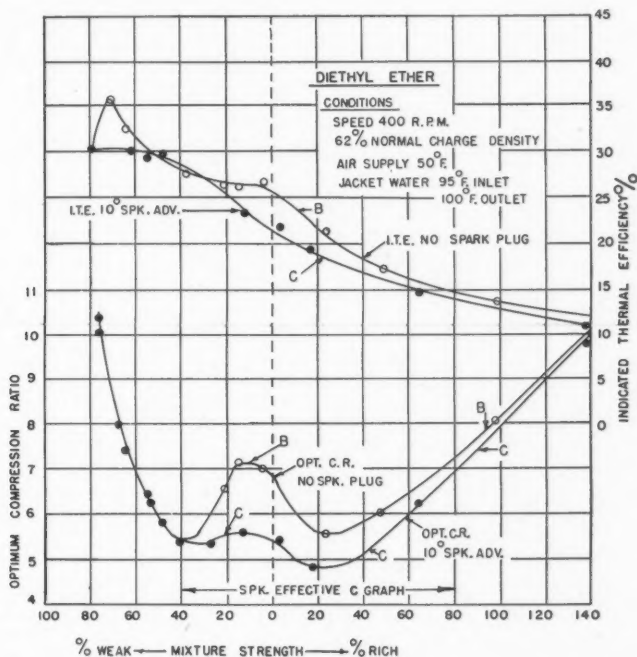


FIG. 4. Diethyl ether. Results obtained with and without spark ignition and in both cases using optimum compression ratio, reduced charge density, and same temperature conditions.

engine. Thus spark ignition failed when the mixture became leaner than 40% weak and the experiment was continued by using compression ignition until the mixture was 75% weak and power output became zero. Spark ignition also failed, as with acetaldehyde, when the mixture became more than 80% rich, and again it was possible to carry on with still richer mixtures by using compression ignition. The *B* and *C* graphs coincide when the mixture is leaner than 40% weak and spark ignition is ineffective but not when the mixture is more than 80% rich and spark ignition again ineffective. It was suggested when describing the similar experiments with acetaldehyde that this rather puzzling phenomenon might be due to the spark plug having an igniting effect independently of the spark. This was found to be so in the course of experiments to be described in another Part. They demonstrate



TABLE III

RELATIVE EFFECTS OF COMPRESSION AND SPARK IGNITION ON INDICATED THERMAL EFFICIENCY (I.T.E.) WITH DIETHYL ETHER AS FUEL, SAME CHARGE DENSITY BOTH CASES

Mixture	Opt. C.R. (spark)	Opt. C.R. (blind plugs)	I.T.E. (spark), %	I.T.E. (blind plugs), %	Observed inc., %	Calculated inc., %
30% weak	5.3	5.7	27	27	0	3.1
10% weak	5.6	7.1	23½	26	10.6	9.5
Correct	5.5	6.8	22	25½	15.8	8.8
20% rich	4.8	5.6	19	21½	13.2	6.9
40% rich	5.2	5.8	17	18½	8.8	4.8

that the ceramic core of an unfired plug, not its points, possesses an igniting effect when ignition is by compression.

Combustion was silent with weak mixtures and as for the spark ignition experiments with aldehyde in similar conditions, it became light only on increasing mixture strength to 80% rich.

The relative effects of compression and spark ignition on thermal efficiency differed from those observed when acetaldehyde was used in that for mixtures ranging from correct to 40% rich the effect of compression ignition was beneficial rather than deleterious. Relevant data are tabulated above.

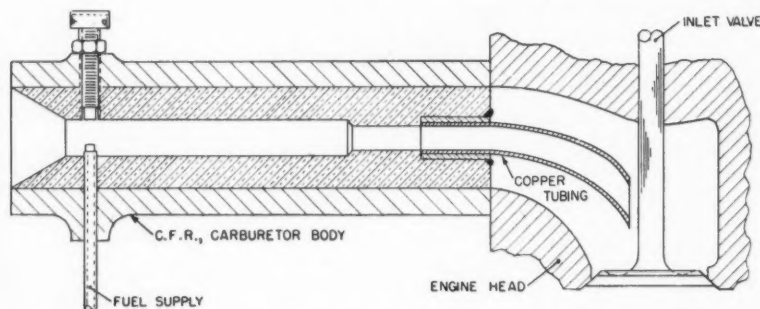


FIG. 5. Carburetor arrangement for experiments with reduced charge density.

#### DISCUSSION

The novel features of the method of experiments described in this Part are the use of the C.R. for optimum timing of either spark or compression ignition and a subnormal charge density in order to prevent knock intensity becoming intolerably severe on increasing mixture strength from very weak to very rich. The experimental arrangements were otherwise similar to those of the experiments on nuclear ignition described in Parts XVI (3), XVII (4), and XVIII (5). That is, the engine was run "cool" at the relatively low speed of 400 r.p.m. and with wet carburetion in order to facilitate the formation of an igniting concentration of nuclei by liquid phase decomposition or cracking of the fuel

and to reduce the tendency of hot surfaces in the combustion chamber to ignite the combustible mixture or to promote preflame oxidation.

The W form of the graphs relating C.R. for optimum compression ignition timing and mixture strength is in general similar to that described by Campbell as having been obtained when using *pentane* in standard knock rating conditions, see discussion of paper on *Precombustion reactions in the spark ignition engine* by Retailliau, Richards, and Jones (9), Standard Oil Development Co. The especially interesting features of Campbell's experiments were the finding that aldehyde was formed in great profusion in mixtures too weak to be ignited by the spark if C.R. were raised to induce greater than "borderline" knock intensity and that compression ignition occurred on further increasing C.R.

The authors of the paper mentioned above consider that during compression, oxidation precedes decomposition. Their experiments were, like those of Campbell, made with a hot engine; the jacket coolant being maintained at 212° F. and the fuel-air mixture raised to 300° F. before entering the cylinder. It would be expected, therefore, that oxidation of fuel on hot surfaces in the combustion chamber would begin immediately on admission of the charge in the conditions of turbulence induced by the passing of the charge with high velocity through the restricted opening of the inlet valve.

Further experiments on precombustion reactions, carried out in the du Pont Petroleum Laboratory, were described by Pastell (7) six months later. A *motored* engine was used with the jacket coolant maintained at 212° F. and the inlet mixture temperature varied over the range 100 to 400° F. A special feature of the experiments was that manifold air pressures were varied over the range 15 to 75 in. Hg. Both oxidation and decomposition must have occurred during compression in the temperature conditions. Oxidation seems to have been regarded as the predominant reaction because the *heat liberated* is taken into account when discussing thermal efficiency, no allowance being made for the heat absorbed by an endothermic decomposition reaction. The hot engine may be regarded as a heated chamber into which reacting mixture is admitted suddenly and its temperature raised by contact with uncooled surfaces and by compression. It is of interest accordingly that the combustion characteristics described by Pastell are in general similar to those determined by Townend (10) when compressed mixture was admitted suddenly to a heated bomb.

Cold fuel-air mixture was admitted into a cool engine in the experiments of this Part and it is considered that decomposition was the primary reaction and provided the nuclei on which oxidation occurred in the body of the mixture. It is difficult to account otherwise for the profuse formation of aldehyde in extremely weak mixtures, as reported by Campbell, and for the fact that such mixtures can be ignited by the heat of compression but not by a spark. What is thus regarded as nuclear ignition was obtained in the experiments described in this Part, with mixtures 75% weak to 140% rich. The range has moreover been extended at both ends. Spark ignition, on the other

hand, was effective only over the mixture range 40% weak to 80% rich. It appears, therefore, that recorded limits of inflammability apply solely to homogeneous gaseous mixtures and that the relatively high rate of flame propagation in engines is due in part to the nuclei always present in some concentration.

Pastell, in the reference quoted, mentions three of the several theories advanced at various times to explain detonation. These may be regarded as the survivors. They are in the order given, the Callendar nuclear theory as modified by King (1, 2), the detonation wave theory, and the autoignition theory which is stated to be the hypothesis most generally accepted. The modified nuclear theory as advanced in Part IV (2) was, as stated by Pastell, based on the assumption that detonation of the end gas would be initiated by nuclear particles of carbon. The assumption was made in respect of unsupercharged carburetor engines using paraffinic fuels for which the C.R. seldom exceeds 7:1. The temperature required for nuclear ignition is then attained in the end gas only and when the mixture is approximately correct. Moreover, the required concentration of nuclei can be formed in the time available only in such mixtures and carbon particles are probably the sole type of nuclei capable of persisting until detonation occurs late in the combustion period. In mixtures even 25% weak, flame movement in the absence of nuclei is relatively slow and exhaust valves are liable to some degree of burning. Compression ignition is a different problem. A relatively high C.R. is required for ignition and combustion must be completed soon after top dead center if an acceptable value of thermal efficiency is to be obtained. The ignition process is that of the Diesel engine and maximum thermal efficiency is obtained with mixtures leaner than the weakest which can be used in the spark ignition carburetor engine operated at a relatively low C.R. The experiments of this and Part XVIII (5), were concerned with compression ignition. There is then no end gas and the results indicate that the nuclei responsible for the ignition of *weak* mixtures may be regarded tentatively until further experiments are completed, as aggregates of condensible products of aldehyde (5, p. 389). Thus deposits seen on the piston after long continued running on very weak mixtures were of a resinous appearance and after similar running on rich mixtures, the piston crown was found to be heavily coated with finely divided carbon. It is indicated accordingly that the autoignition obtained by compression was a nuclear effect.

#### ACKNOWLEDGMENTS

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## THE OXIDATION, DECOMPOSITION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

### XX. THE ADVERSE EFFECT ON THERMAL EFFICIENCY OF THE ENDOTHERMIC REACTION REQUIRED FOR NUCLEAR IGNITION AS SHOWN BY ENGINE EXPERIMENTS WITH METHANOL, ACETALDEHYDE, AND DIETHYL ETHER<sup>1</sup>

BY R. O. KING<sup>2</sup> AND A. B. ALLAN<sup>3</sup>

#### ABSTRACT

Autoignition in engines may, depending on compression ratio and the nature of the fuel, occur before, after, or without spark ignition and is due, according to the Nuclear Theory as stated in Part IV, to the heat of oxidation reactions on material particles formed by the cracking of the fuel. Cracking is an endothermic reaction and the consequent absorption of heat in the gaseous phase would be expected to result in a lower thermal efficiency than would otherwise be obtained. The results of experiments with methanol, acetaldehyde, and ether have been used in this Part in an endeavor to verify the validity of the theory. Thus, methanol cannot be decomposed in the engine to the extent necessary for the formation of material nuclei and autoignition was not obtained. Acetaldehyde and ether decompose relatively easily and autoignition occurred at relatively low compression ratios. Corresponding thermal efficiencies are exhibited by a series of graphs which show the extensive deviations from ideal efficiencies observed when acetaldehyde and ether were used as fuels compared with that observed when methanol was used. The deviations are as would be expected taking heat of activation into account and it is indicated that in most cases a pressure wave is required for the nuclear ignition of other than a small volume of unburned mixture remaining late in the period of combustion when the ignition is by spark. The experiments described are in respect of an hitherto unexplored aspect of the nuclear theory of ignition and are to be regarded as preliminary to more detailed ones with hydrocarbon fuels.

#### INTRODUCTION

The experiments with acetaldehyde and diethyl ether described in Part XIX (6) were carried out with reduced charge densities and with a carburetor type engine operated at relatively low temperatures. It was possible in the conditions to use either spark or compression ignition and to adjust the compression ratio to the value required for maximum power output with any mixture strength without causing an intolerable intensity of knocking combustion. It appeared to be possible, in the circumstances, to determine the effects of the individual limiting factors on engine performance in terms of power and thermal efficiency. Detonation with some fuels and preignition with others are the important factors.

The hypothesis that detonation in a carburetor type spark ignition engine is due to the igniting effect of nuclei formed by decomposition (cracking) of the fuel at the high temperature and pressure attained by the last part of the

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fuel-air mixture to burn was advanced in Part IV (5). This decomposition is an endothermic reaction and the heat absorbed accordingly would be expected to affect thermal efficiency adversely. The adverse effect would be inappreciable if the reaction occurred solely in a small part of the combustible mixture which remained unburnt late in the combustion period. The effect would, however, become greater as the end gas increased in volume with increase of compression ratio and would attain a maximum value when the whole mixture became in effect the end gas.

The idea that an endothermic reaction may occur in the combustible mixture is not novel. The reaction was suggested by Callendar over forty years ago, in a paper on "the effect of size on the thermal efficiency of engines," as possibly one of the factors which prevent air standard efficiency being attained in a real engine (1, p. 226). The possibility does not seem to have been investigated experimentally. Dissociation and the change in the ratio of the specific heats with increase of mixture strength are the sole effects commonly taken into account when calculating the ideal efficiency of a real engine. These effects occur in respect of the products of combustion and on this basis it is solely the expansion ratio which controls thermal efficiency.

If, however, endothermic reactions are taken into account, efficiency may vary also with the liability of the fuel to decomposition by the heat of compression.

When acetaldehyde and diethyl ether were used as fuels in the conditions of the experiments described in Part XIX (6), the thermal efficiency failed to change as it would if expansion ratio were the sole governing factor. The failure is attributed, according to the nuclear theory, to the heat absorbed by endothermic reactions which occurred prior to the completion of combustion and therefore prior to expansion because the timing of ignition, whether by spark or compression, was always adjusted to the optimum value.

It appeared that the approximate magnitude of the adverse effect could be demonstrated by a determination of the difference between thermal efficiencies obtained with the detonating fuels acetaldehyde and diethyl ether, and that obtained when using a nondetonating fuel. Methanol was selected accordingly for experiments to be made in conditions similar to those used for the experiments with acetaldehyde and diethyl ether described in Part XIX. The three fuels contain oxygen in the molecule and all are reputed to be unusable alone for a carburetor engine as usually operated.

The characteristics of methanol as a fuel are the opposite to those of diethyl ether. Thus it is stated frequently that the ether will detonate but not preignite and that methanol will preignite but not detonate. It is also of significance in respect of nuclear ignition that the alcohol burns with a smokeless blue flame when mixed with air in any proportion, whereas only weak mixtures of acetaldehyde or ether with air burn similarly and both substances knock violently when used in normal conditions of engine operation. Ethyl alcohol, 95% ethanol, would have served equally well. There is, however, a great deal



of information available concerning that substance when used as the sole fuel for an engine but extremely little about methanol. Ricardo (8, p. 144), in the course of experiments for the Empire Fuels Committee, tried methyl alcohol, "purified wood spirit", as a fuel for the *E 35* engine and found that preignition occurred when the highest useful compression ratio (H.U.C.R.) was 5:1. The engine speed was 1500 r.p.m., the jacket coolant 140° F., and the heat input to the mixture equivalent approximately to that added by a water heated induction system. Synthetic methyl alcohol (methanol) was probably not available at the time of the experiments mentioned and although a great deal of work has since been done in respect of substitute fuels, few references have been found to experiments with methanol as the sole fuel for a carburetor engine; those by Wiebe and Porter, for example, were made with mixtures of the substance with water (13). The feature of importance for present purposes is, however, that spark ignition was always used and that a limitation of heat load was required to prevent preignition.

#### ARRANGEMENTS MADE TO PROVIDE THE CONDITIONS OF EXPERIMENT

The experiments with methanol were made with a C.F.R. *F. 2.* engine and the auxiliary equipment was as described at some length in Part XIX. The air entering the carburetor was maintained at 50° F., the cooling water entered the cylinder jacket at 95° F. and left the cylinder head jacket at 100° F. The carburetor, as before, was fitted with a  $\frac{1}{4}$  in. diameter choke tube which reduced the charge density to approximately 65% of normal with an engine speed of 400 r.p.m. The lubricating oil, S.A.E. 10, in the crank case, was maintained at 120° F.

Technical grade methanol, reputed to be better than 99% pure, was used for the experiments. The boiling point was found not to differ appreciably from that of the pure substance, namely, 64.7° C. (148.3° F.).

A collection is given below of data relative to the three fuels used in this Part to demonstrate the apparent effect of endothermic reactions on thermal efficiency.

TABLE I  
DATA IN RESPECT OF METHANOL, ACETALDEHYDE AND DIETHYL ETHER

	Methanol, CH <sub>3</sub> OH	Acetaldehyde, CH <sub>3</sub> CHO	Diethyl ether, (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O
Boiling point	64.6° C., 147° F.	21° C., 69.8° F.	34.6° C., 94.4° F.
Correct A/F, by weight	6.47:1	7.84:1	11.27:1
Lower calorific value, B.T.U./lb.	9100	10550	14567
B.T.U./cu. ft., correct mixture at N.T.P.	96.7	103.0	108.5
Heat of vaporization, B.T.U./lb.	475	245	151
"E", energy of activation, gm-cal./gm-mol.	68000	46000	67000
"E", B.T.U./lb.	3820	1880	1630
Lower limit of inflammability % vapor in mixture with air	6.7	4.0	1.85



The values of "E" given in Table I are those determined by Stavely and Hinshelwood at subatmospheric pressures by the bulb method (10, p. 1568). In order to provide a basis for discussion they may be regarded as relative values in respect of the initiation of decomposition as it occurs in an engine.

The values given in Table I for lower limits of inflammability are for mixtures ignited by spark in closed vessels as given by Coward and Jones (2).

#### EXPERIMENTAL RESULTS. METHANOL

When describing and discussing experimental results, the term "compression ratio" will be abbreviated to the initial letters C.R. and diethyl ether described as ether.

Spark ignition was always necessary for the experiments with methanol. Timing was fixed at  $10^\circ$  advance, as for the experiments with acetaldehyde and ether, and C.R. was always adjusted to an optimum value as mixture strength was varied. Spark ignition was fully effective solely for mixtures richer than 30% weak. The engine would run on somewhat weaker mixtures

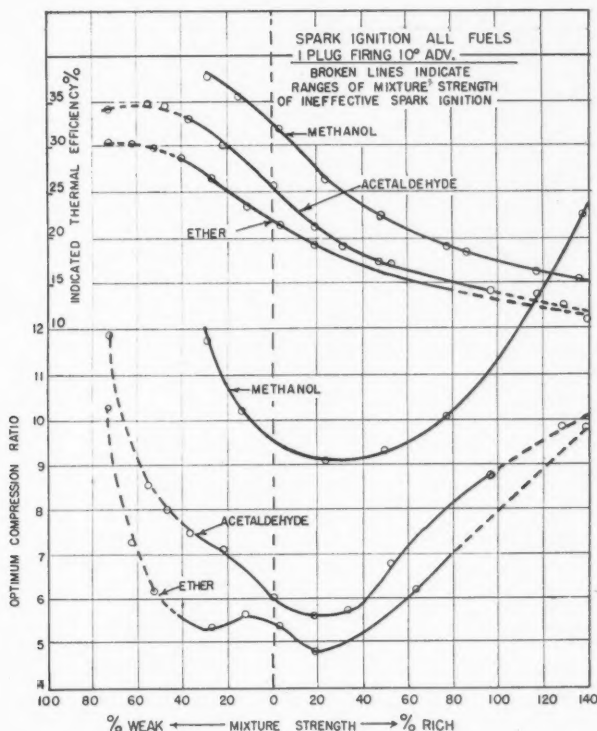


FIG. 1. Optimum compression ratio, thermal efficiency, and related mixture strength. Solid lines indicate spark ignition, broken lines compression ignition.

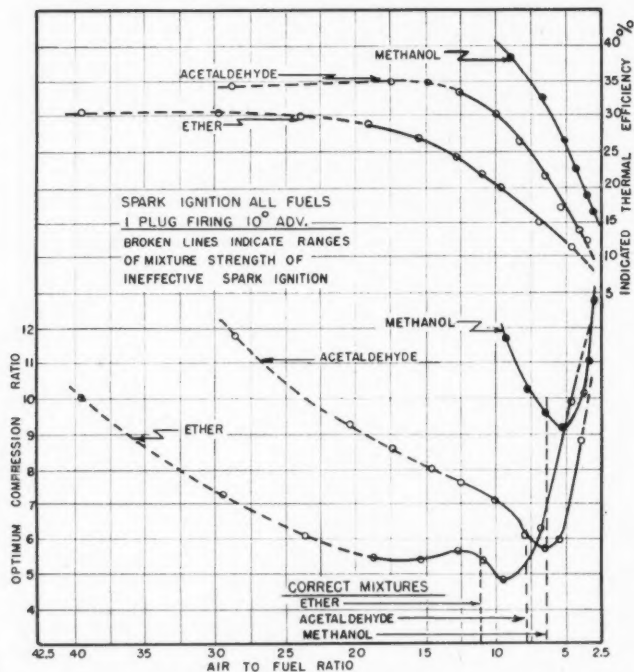


FIG. 2. Optimum compression ratio, thermal efficiency, and related air to fuel ratio. Solid lines indicate spark ignition, broken lines compression ignition.

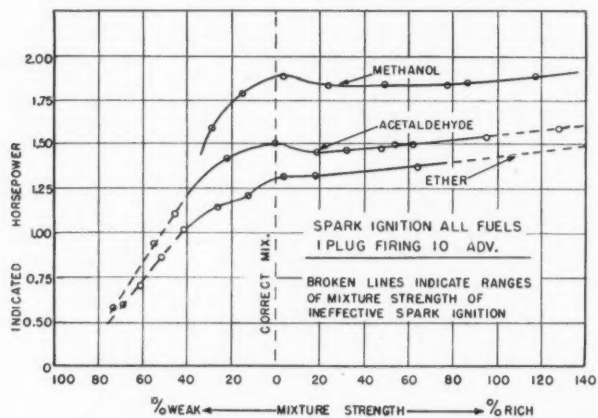


FIG. 3. Relation between power and mixture strength with conditions as used Figs. 1 and 2.

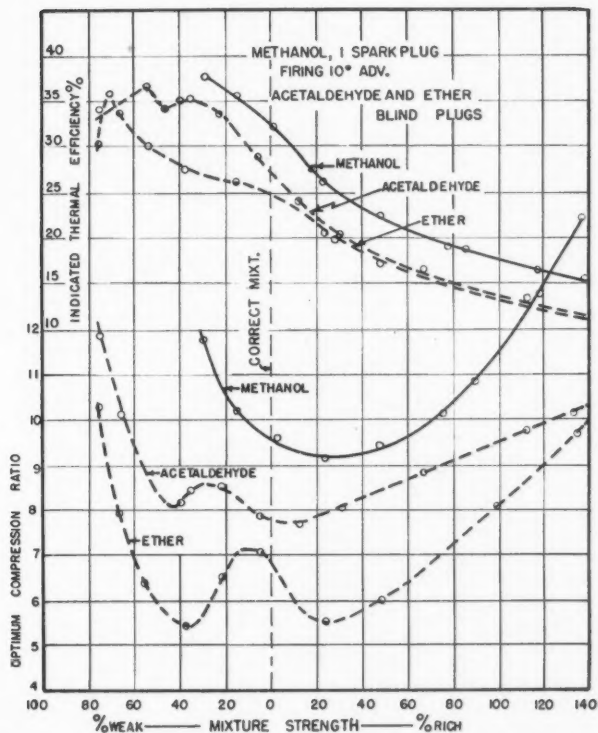


FIG. 4. Optimum compression ratio, thermal efficiency, and related mixture strength; spark ignition for methanol, compression ignition for acetaldehyde and ether.

but ignition became irregular and power diminished rapidly. Attempts to run the engine with ignition by compression always failed although occasional violent explosions occurred when C.R. was increased to 18:1 with a correct mixture or to 25:1 with a mixture 30% weak.

At optimum C.R. combustion was just audible over the mixture range to 100% rich and silent with richer mixtures.

The graphs illustrating the combustion characteristics of methanol are presently given together with similar ones for acetaldehyde and ether as reproduced from Part XIX (6). Experimental results obtained with spark ignition are shown by solid line graphs and those with compression ignition by broken line graphs, in an endeavor to avoid confusion. Two sets of graphs are presented.

The experimental results for methanol are shown by both sets in order to facilitate comparisons. One set, Figs. 1 to 3, shows, in addition, the results of the experiments of Part XIX with acetaldehyde and ether obtained when

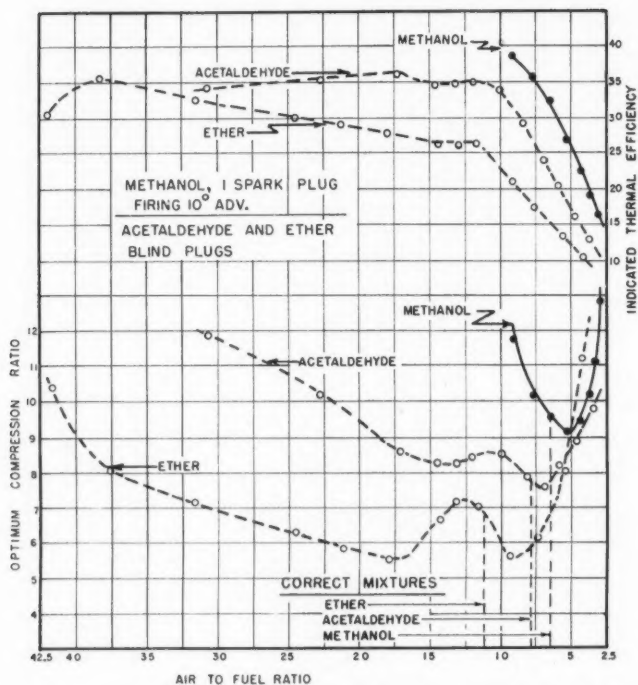


FIG. 5. Optimum compression ratio, thermal efficiency, and related air to fuel ratio; spark ignition for methanol, compression ignition for acetaldehyde and ether.

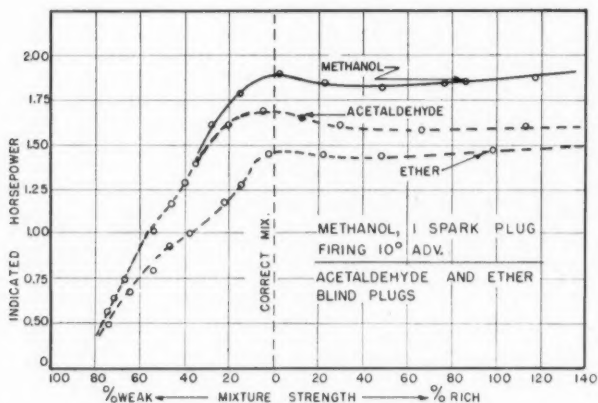


FIG. 6. Relation between power and mixture strength with conditions as used for Figs. 4 and 5.

a single spark plug was used; the spark being effective over that part of the mixture strength range indicated by the solid lines of the graphs. The other set, Figs. 4 to 6, also shows comparable results of experiments with the three fuels but when blind plugs only were fitted to the engine for the experiments with acetaldehyde and ether.

The graphs of Fig. 2 of the first set and those of Fig. 5 of the second set are plotted on a base of air to fuel ratio by weight. This commonly used method of plotting extends the graphs on the weak side of the correct mixture and foreshortens them on the rich side. The method of plotting is therefore useful in displaying the characteristics of the ignition and combustion of weak mixtures although a single datum line for correct mixture cannot be set out for the three fuels concerned.

The volumetric efficiency at the constant engine speed of the experiments and with the fixed diameter carburetor choke tube would normally be affected by the varying heats of vaporization of the fuels used. It should, on this basis, be a maximum with methanol and a minimum with ether, see Table I. The vessel containing the air cooling coils was, however, interposed between the air metering orifice and the carburetor and the consequent restriction of the air supply to the engine varied according to the extent to which the air passageways in it were blocked by frost. This in turn varied with atmospheric humidity. The cooling coils were always defrosted on completing a "run" which, however, including the warming up period, generally required about eight hours. It was not practicable to interrupt a run in order to defrost. The consequent variation of the restriction due to frost was sufficient to mask the change of volumetric efficiency due to differing heats of vaporization. The effect on volumetric efficiency of vaporization in the cylinder was further masked by that which occurred when the wet moisture formed in the carburetor was discharged through the curved choke tube directly onto the inlet valve (see Fig. 5, Part XIX). The factors mentioned above were taken into account by measurement of the rate of air aspirated by the engine and on this basis, the total variation of volumetric efficiency was 5% at correct mixture strength and the maximum value was not always obtained when using methanol as the fuel. The variation is not significant in respect of indicated thermal efficiency. The average volumetric efficiency was 65% of the normal value regarded as being that obtained when the standard C.F.R. carburetor is used.

The power developed when using the three fuels in the conditions of the experiments, Figs. 3 and 6, attained a distinct maximum corresponding to the correct mixture when the acetaldehyde or ether was ignited by compression, Fig. 6. The maximum values were less distinctly marked when the substances were ignited by spark as shown by the graphs of Fig. 3. The tendency of indicated horsepower to rise or to remain nearly constant as mixture strength exceeded 30% rich is attributed to the C.R. being raised accordingly and always to an optimum value. The existence of a maximum I.H.P. at correct mixture strength is also attributed to the optimum C.R. having been used.

Indicated horsepower as given by the graphs of Figs. 3 and 6 can be converted to I.M.E.P. by using the factor 53.0. Thus at correct mixture strength the I.M.E.P. when using methanol was 102 lb. per sq. in. The values for acetaldehyde and ether were 89.5 and 77.5 respectively when ignition was by compression, Fig. 6. They were 79.5 and 70.5 respectively with spark ignition, at the necessarily lower values of optimum C.R., Fig. 3.

#### DISCUSSION

##### *The Lower Limit of Inflammability, Spark Ignition*

The lower limits given in Table I for methanol, acetaldehyde, and ether are for percentage concentration of vapor in a mixture with air. They were determined at atmospheric pressure with ignition by spark, in closed vessels. It is of interest to compare them with the values obtained with spark ignition when the mixtures were used in an engine at relatively high temperatures and pressures. The lower limit for acetaldehyde or ether was then attained when mixtures with air became leaner than approximately 40% weak. The exact limiting value was difficult to determine because of the overlapping of spark and compression ignition. When methanol was used as the engine fuel, ignition by spark became irregular when the mixture was leaner than 30% weak and ignition did not occur by compression. The engine continued to run unsteadily on mixtures somewhat leaner than this but power diminished rapidly even on increasing the C.R., probably because, after missing began, the clearance volume could have contained either unburned mixture or products of combustion. Comparable values of lower limits are tabulated below.

TABLE II  
LOWER LIMITS (L.L.) OF INFLAMMABILITY OF MIXTURES WITH AIR,  
OF METHANOL, ACETALDEHYDE, AND ETHER, WITH SPARK IGNITION

	CH <sub>3</sub> OH	CH <sub>3</sub> CHO	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O
L.L. (Table I) % concentration in air	6.7	4.0	1.85
L.L. (engine) % in mixture supplied	12.0	4.8	2.03
L.L. (engine) % in ignited mixture taking residual gas as air	9.0	4.2	1.72
Compression ratio at ignition	11.7	7.5	5.5

When correcting for the volume of residual gas added to the aspirated mixture before spark ignition, compression ratio only was taken into account. Thus no allowance was made for the difference in temperature and pressure between it and the mixture as admitted nor for the gas being, in part, products of combustion. These corrections if they could be made would extend the lower limit of inflammability to the least extent for methanol, ignited at a C.R. of 11.7 and to the greatest extent for ether, ignited at a C.R. of 5.5. Thus the corrections would extend the lower limit for ether to a value less than 1.72 which even without the corrections is less than the value of 1.85 given in Table I. The relatively high temperatures and pressures in the engine appear therefore to cause the greater increase in inflammability with the detonating fuels.



*Ideal Efficiency Compared with the Value Observed with Methanol as a Fuel*

Values for ideal efficiencies of real engines as given in works of reference are calculated as being those attainable when the working fluid contains products of combustion of the fuel and depend accordingly on expansion or compression ratio if the two are equal and on the concentration of fuel in the mixture with air. The effect of fuel concentration on efficiency depends then on the specific heats of the products of combustion, taken over the temperature range of expansion and the dissociation which may occur at temperatures of combustion. The value of " $n$ " in the expression  $\left(\frac{1}{r}\right)^n$  is reduced accordingly as the concentration of fuel increases, with the consequence that thermal efficiency, as given by the expression  $1 - \left(\frac{1}{r}\right)^n$ , diminishes.

Computations of ideal efficiencies present many difficulties but were made by Tizard and Pye (12, p. 13) for mixtures of air with benzene, with compression ratios\* rising from 4 to 10 and based on values of specific heats available at the time. A partial revision was made by Pye (7, p. 181) when more accurate data for specific heats at high temperatures became available. The probable typographical error in the equation given for efficiency should be noted. The graphs obtained accordingly for the relations between efficiency and compression ratio for three mixture strengths have been extended to a compression ratio of 20 and by interpolation to include graphs for mixtures 75% weak and 10% rich (see Fig. 7). The extension to a C.R. of 20 is necessary because the C.R. used for experiments of the present series frequently approaches that value. Graphs for additional mixture strengths are necessary in order to obtain a sufficient number of points on a single graph when both C.R. and mixture strength are variables.

The ideal efficiencies given by the graphs of Fig. 7 are based on the thermodynamic properties of the combustion products of a hydrocarbon and may not be strictly applicable to the results of experiments with methanol as the fuel for an engine. It may safely be assumed, however, that graphs for ideal efficiencies when methanol is used, and calculated similarly, would merely be displaced to some extent from those for benzene, Fig. 7, the form being unaltered.

A comparison is given accordingly by the graphs of Fig. 8, of ideal efficiencies, with those observed when methanol was used as the fuel for the C.F.R. engine. Methanol is a nondetonating fuel because, according to the nuclear theory, it cannot be decomposed in the engine to the extent necessary for the formation of nuclei of ignition. Spark ignition is therefore always necessary and the graph for observed efficiencies is of the same general form as that for ideal values but not parallel to it. Thus it will be noted that the departure of observed from ideal efficiency increases with increase of compression ratio, as would be expected because of the extent of decomposition increasing accord-

\* Compression and expansion ratios have equal numerical values in piston engines as generally constructed.



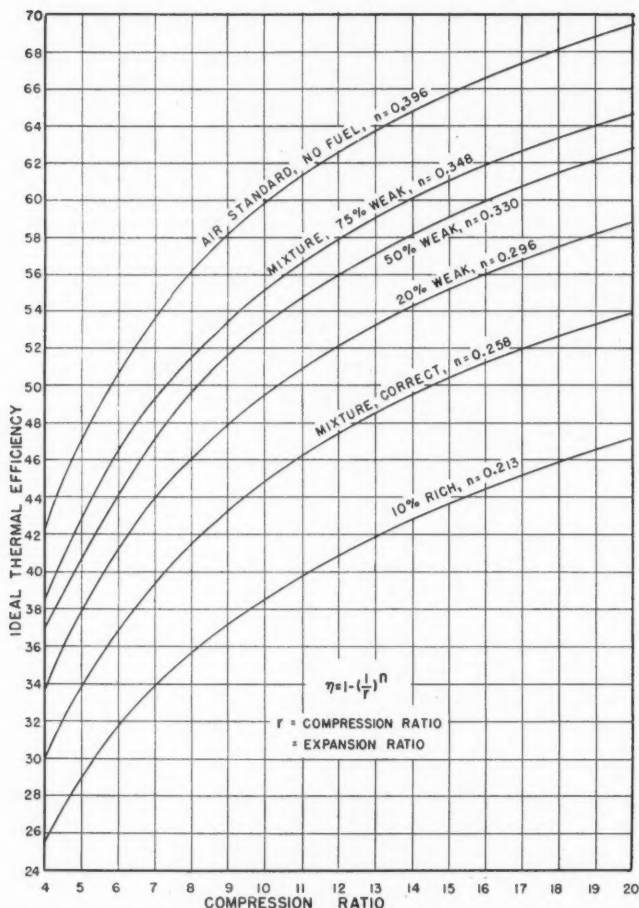


FIG. 7. Relation between ideal efficiency and compression ratio as affected by mixture strength, according to ordinary rules of calculation.

ingly. Methanol is known to decompose in stages and according to Fletcher (4),



An endothermic reaction is therefore possible in the engine and the first stage would yield volumes of hydrogen and formaldehyde each equal to the volume of the methanol vapor before decomposition; the second stage provides two volumes of hydrogen and one of carbon monoxide. Formaldehyde is not a proknoock according to recent experiments by Downs, Walsh, and Wheeler (3, p. 480) and carbon monoxide cannot be dissociated at engine temperatures to yield the carbon required for nuclear ignition. The hydrogen formed profusely even by the first stage of decomposition may safely be assumed to

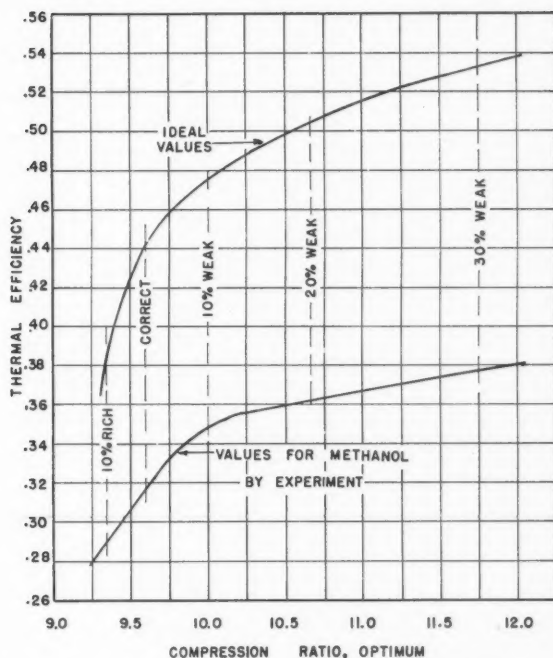


FIG. 8. Values of ideal efficiency from Fig. 7, compared with values observed when using methanol.

account for the preignition which limits the C.R. at which methanol can be used in the ordinary temperature conditions of engine operation.

#### *Comparable Thermal Efficiencies. Methanol, Acetaldehyde, and Ether*

It is shown by the graphs of Fig. 8, for experiments with methanol, a non-detonating fuel, that thermal efficiency *tends* to vary with C.R. and mixture strength in accordance with the ordinary rules of calculation which take into account postcombustion effects only. The lack of complete accord is attributed to some degree of decomposition occurring prior to the completion of combustion with a consequent irrecoverable loss of heat. A greater lack of accord would be expected when using detonating fuels, according to the nuclear theory of ignition, because of the necessarily greater degree of decomposition. The expectation is confirmed by the experimental results exhibited by the graphs of Figs. 9 to 12 for the efficiencies observed when using acetaldehyde and ether as compared with that observed when using the nondetonating methanol.

Thermal efficiencies given by the graphs are indicated values taken from Figs. 1 and 4, but instead of being plotted against mixture strength are, as for Fig. 8, plotted against optimum compression ratio with values increasing as

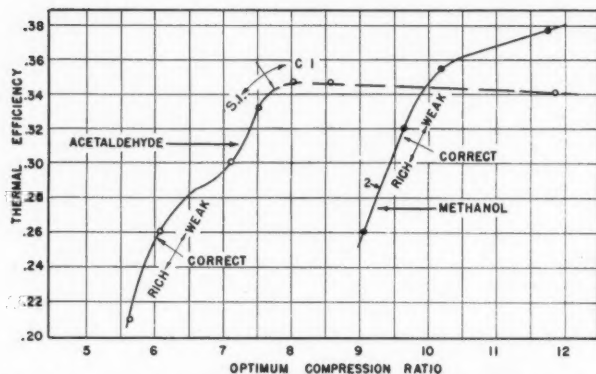


FIG. 9. Methanol and acetaldehyde. Observed relation between thermal efficiency and optimum compression ratio; methanol ignited by spark, acetaldehyde ignited by spark over range of mixture strength indicated by solid line part of graph and by compression as shown by broken line part.

mixture strength decreases. Spark ignition is indicated as having been used when the graphs are solid lines. Broken lines indicate ignition by compression and the changeover from spark to compression ignition obtained when using aldehyde or ether at lower compression ratios than required for compression ignition is also marked on the graphs by arrows pointing to compression ignition, C.I., or to spark ignition, S.I. Especially noteworthy features exhibited by the graphs are as follows:

(1) The great *deviation* of the detonating fuels acetaldehyde and ether as compared with that of the nondetonating fuel methanol, from the ideal relation between thermal efficiency and compression ratio, as calculated by

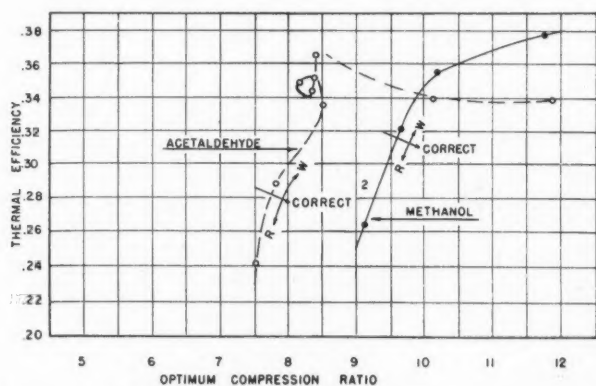


FIG. 10. Methanol and acetaldehyde. Observed relation between thermal efficiency and optimum compression ratio, acetaldehyde ignited by compression, methanol by spark.

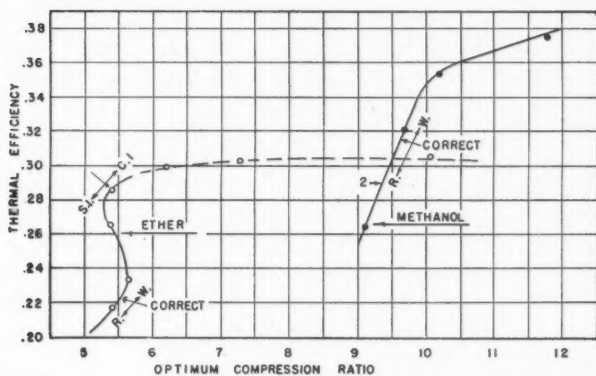


FIG. 11. Methanol and ether. Observed relation between thermal efficiency and optimum compression ratio; methanol ignited by spark, ether by spark over range of mixture strength indicated by solid line part of graph and by compression as shown by broken line.

taking into account effects occurring only after completion of combustion. The deviation is greater for ether than for acetaldehyde which detonates less readily.

(2) The graphs, especially those for acetaldehyde and ether, indicate two phases of ignition. The indication is more pronounced for ether than for acetaldehyde. It is also the more pronounced at the higher compression ratios used to obtain compression ignition over the mixture range 40% weak to 80% rich. Thus the loops shown by the graphs of Figs. 10 and 12 are believed to be coincident with the change from one phase of ignition to another. The changeover, Figs. 9 and 11, is marked by the pronounced in-

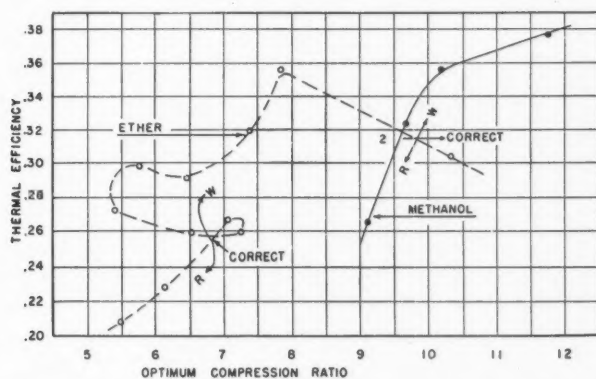


FIG. 12. Methanol and ether. Observed relation between thermal efficiency and optimum compression ratio, ether ignited by compression, methanol by spark.

flection which occurs when spark ignition ceases to be effective and is succeeded by compression ignition.

(3) The thermal efficiencies observed with compression ignition when a spark plug is in place but not fired, differ in magnitude and pattern from those obtained with compression ignition when all plugs are mild steel blanks. The difference is more pronounced for ether than for acetaldehyde (compare second phases of ignition, Figs. 9 and 10 for acetaldehyde with Figs. 11 and 12 for ether).

#### *The Nuclear Theory of Ignition and Endothermic Decomposition Reactions*

It is essential to the nuclear theory as stated in Part IV (6) that fuels subject to detonation in an engine decompose to provide material nuclei on which oxidation reactions can occur in an air-fuel mixture. That is, decomposition must precede oxidation. Decomposition of the fuels in an engine is an endothermic reaction and the validity of the nuclear theory is believed to be confirmed by the occurrence in engine experiments of a corresponding loss of thermal efficiency.

A fuel molecule has a definite probability of decomposing to others of lower molecular weight if it acquires energy equal to or greater than the "energy of activation", which is given in terms of gram-calories per gram-mole and designated by the symbol " $E$ ". The temperature at which decomposition begins depends on the stability of the molecule and the value of  $E$  diminishes with increase of pressure. The percentage decomposition increases with time of exposure to the temperature and pressure conditions for which  $E$  has a particular value. That is, a continuous absorption of heat is required to maintain the decomposition reaction. If it be carried out at the temperature required for its initiation, the products are in large part unsaturateds containing fewer carbons in the molecule than were contained in that of the parent substance. The velocity of the reaction increases rapidly with increase of temperature above that required for its initiation. Unsaturateds are then formed at a decreasing rate; carbon, lower saturateds, and hydrogen at an increasing rate.

$E$ , for a particular substance, has a maximum value when the decomposition reaction is homogeneous. Lower values are obtained if the surface of the reactor in which decomposition occurs is such that the reaction becomes in part heterogeneous. Values of  $E$  given in works of reference have usually been determined in quartz reactors at subatmospheric pressures and are reputed to be for homogeneous reactions. They cannot be applied quantitatively to decomposition reactions which occur at the relatively high pressures in the combustion chamber of an engine which contains various metal surfaces heated unequally when power is being developed. The values of  $E$ , Table I, may however be used to indicate the relative tendencies of methanol, acetaldehyde, and ether to decompose in an engine. The relative weights of the substances in correct mixtures with air are the reciprocals of the air-fuel ratios given in Table I and if multiplied by the respective B.T.U. values per pound

required to initiate decomposition give relative values for the heat required for decomposition in the engine as below:

Methanol	592
Acetaldehyde	242
Ether	145

According to the nuclear theory, the relative values may be taken to represent the antiknock properties of the fuels and are in agreement with experimental results, remembering that methanol decomposes to yield hydrogen in a concentration sufficient to account for preignition in a hot engine and that this occurs prior to the formation of nuclei.

#### *Nuclear Ignition as Promoted by Pressure Waves*

The decomposition by a single application of pressure of the whole of the fuel in a mixture with air in an engine, to the extent required to produce a uniform igniting concentration of nuclei throughout the mass, would require a relatively large quantity of heat and the resulting detonation would probably be disastrous. In practice either in engines or in compression ignition machines, temperature in the combustible mixture is not uniform on completion of compression. In an engine using liquid fuels, mixture strength also is not uniform. Thus decomposition can occur preferentially in one or more small parts of the compressed mixture and provide therein the concentration of nuclei required for autoignition. One or more pressure waves could then be generated which on passing through a mixture already heated by compression would raise it progressively to the higher temperature required for decomposition and consequent nuclear ignition. The rate of flame propagation in the major portion of the combustible mixture would then be the resultant of the pressure wave velocities. Thus it appears to be possible to create pressure waves which will detonate the mixture in the combustion chamber of an engine without the preliminary length of flame "run" which is otherwise necessary.

The creation of a pressure wave in the *end gas* is discussed by Serruys (9). He postulates that at one place or another the end gas will have a point at a maximum temperature and that a small globular region around the point will have a uniform temperature and pressure which will increase as the flame front advances until autoignition occurs and starts a pressure wave which will pass through and ignite the remainder. It is further suggested that the temperature level in the globule may be such that the majority of hydrocarbons are cracked before self-ignition occurs and that the newly formed molecules will the more readily combine with oxygen. Serruys appears to envisage the formation of nuclei of gaseous globules and applies his hypothesis solely to the part of the charge remaining unburned after flame has been initiated by a spark. Nevertheless, the hypothesis of Serruys in respect of the creation of a pressure wave does not differ in principle from that advanced in this Part. The two differ mainly in respect of the degree of decomposition required to cause ignition.

A pressure wave is not required for the production of the concentration of



nuclei necessary for the autoignition of a small quantity of end gas in a spark ignition engine because the necessary temperature and pressure conditions have been obtained correspondingly late in the period of combustion. A pressure wave would be created but would then pass through a mixture in which combustion was far advanced. The sole effect would be to hasten the process. An explanation is obtained accordingly for the appearance of flame in the whole of the mixture nearly simultaneously with detonation by the end gas. If, however, the end gas were of relatively large volume or if the whole of the charge were to be ignited by compression, the function of the pressure wave would be to produce nuclei of ignition as it passed through a combustible mixture which had not been raised to the necessary extent by compression to the pressure and temperature required for decomposition of the fuel to an advanced stage.

Decomposition by a pressure wave of a hydrocarbon fuel in a compressed mixture with air, to the extent necessary to release copious quantities of free carbon, was mentioned by Miller in the discussion of the paper on ignition by compression by Taylor and others (11, p. 273) as having been demonstrated by himself and his associates, with the aid of high speed photography. This work together with the experimental results for compression ignition described in the paper which Miller discussed is of especial interest in respect of further experiments on the causes of ignition of hydrocarbon fuels which will be described in subsequent Parts.

#### ACKNOWLEDGMENTS

The experiments described in this Part were carried out in the Department of Mechanical Engineering, University of Toronto, with the co-operation of Prof. E. A. Allcut, Head of the Department and with the assistance of Mr. J. C. Junkin, demonstrator and research assistant in the Department.

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## NOTE

**Sulphur Analysis of Canadian Erucic Acid Oils\***

Sulphur compounds of *Brassica* seeds are reported to be undesirable nutritionally (1, 2), and could possibly impart odors and flavors to the extracted oils. Since Canadian erucic acid oils of this type may be used for food (4), it was considered advisable to investigate their sulphur content.

Standard methods of sulphur analysis proved unsatisfactory when applied to the oils. Ignition methods applicable to coal and fertilizer gave low recoveries with added volatile sulphur compounds, and digestion methods used for rubber did not completely destroy the organic matter even after prolonged treatment. Bomb ignition, commonly used with petroleum oils, did not always give complete combustion with crude erucic acid oils.

Commercial availability of highly concentrated hydrogen peroxide (5) suggested its use as a preliminary oxidant of volatile sulphur compounds, followed by ignition with strong alkali, solution in hydrochloric acid, and turbidimetric determination of sulphur as sulphate. This procedure gave recoveries of 96 to 100% of sulphur compounds (allyl isothiocyanate, allyl sulphide, allyl thiourea, carbon disulphide, cystine, sulphanilic acid, thiophene, thiourea) added to refined, sulphur-free vegetable oils. As in other procedures (3), recovery of sulphones, e.g., sulphonol, was low (80-95%) but their presence in vegetable oil sources is unlikely.

*Procedure:*—Pipette 5-10 ml. of oil from closed container into a weighed 50 ml. volumetric flask, and stopper at once. Weigh, add 25 ml. of a cold mixture of seven parts glacial acetic acid and three parts 90% hydrogen peroxide, and replace stopper after moistening it with the solution. *Precautions in handling 90% hydrogen peroxide are described elsewhere* (5). Shake the flask gently until any initial heat of reaction is dissipated, then agitate overnight at sufficient speed to keep the oil phase dispersed. Make to volume with isopropyl ether and mix. Using safety device, pipette a 1-10 ml. aliquot slowly into 3 gm. of reagent chip sodium hydroxide in a 30 ml. nickel crucible. When frothing has subsided add 2 gm. of reagent light magnesium oxide. Place crucible in a cold muffle furnace, and raise the temperature in one hour to 750° C. Ignite two hours at 750° C., cool, and place in 400 ml. beaker with watch glass cover. Add 200 ml. of 1 N hydrochloric acid, stir until frothing ceases, then boil gently until the material is dissolved. Filter the solution through Whatman No. 40 paper into a 200 ml. volumetric flask, washing beaker and crucible with N/10 hydrochloric acid. Make

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to volume and determine sulphur turbidimetrically after addition of barium chloride. Check result with standard curve prepared by turbidimetry of known amounts of sodium sulphate in a solution containing the same amounts of sodium hydroxide, magnesium oxide, and hydrochloric acid as used in the determination. Correct for blank determination.

Application of the above method to crude erucic oils (fanweed, mustard, rape, and mixed weed) showed sulphur contents of less than 0.001%. Alkali refined and bleached oils had no detectable sulphur content. Thus it appears that sulphur originally present in the seeds is lost during oil extraction or remains in the seed cake and will not interfere with utilization of these oils for food.

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